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(INCORPORATED)

Vol. 104

INSTITUTE OF METALS DIVISION

1933

PAPERS AND DISCUSSIONS PRESENTED BEFORE THE DIVISION AT MEETINGS HELD
AT BUFFALO, OCTOBER, 1932 AND AT NEW YORK, FEBRUARY, 1933, WITH
ABSTRACTS AND DISCUSSIONS OF SOME PAPERS ON GASES IN
METALS PRESENTED IN FEBRUARY, 1932

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Notice

This volume is the seventh of a series constituting the official proceedings of the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers. It deals with nonferrous metals and includes papers presented at the Buffalo Meeting, Oct. 3–7, 1932, and the New York Meeting, Feb. 20–23, 1933; together with abstracts of four papers on Gases in Metals presented in February, 1932.

The series is a continuation of the publications and proceedings of the Institute of Metals Division. The complete list of publications and proceedings, including the present volume, is as follows:

1908–1911	*Transactions* of the American Brass Founders' Association: 1908, Vols. 1 and 2; 1909, Vol. 3; 1910, Vol. 4; 1911, Vol. 5.
1912–1916	*Transactions* of the American Institute of Metals, Vols. 6–10.
1917–1918	*Journal* of the American Institute of Metals, Vols. 11–12.
1919–1926	TRANSACTIONS of the American Institute of Mining and Metallurgical Engineers, Volumes 60, 64, 67, 68, 69, 70, 71 and 73.
1927–1928	PROCEEDINGS of the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers, two volumes, of which the latter is now designated Vol. 78 of the A. I. M. E. TRANSACTIONS.
1929–1933	TRANSACTIONS of the American Institute of Mining and Metallurgical Engineers, Volumes 83, 89, 93, 99 and 104, Institute of Metals Division.

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FOREWORD

The present volume of the Transactions is the seventh in the Institute of Metals series. In addition to papers presented at the October (1932) meeting held in Buffalo, and the February (1933) meeting in New York, it contains the annual lecture (February) of the Division, by Dr. Georg Masing, and a copy of the latest revision of the Division's By-laws approved by the Board of Directors of the American Institute of Mining and Metallurgical Engineers April 20, 1933. This volume also contains abstracts of four papers on gases in metals sponsored by the Institute of Metals Division at a joint session with the Iron and Steel Division, held in February, 1932.

That the high standard of quality and wide diversification of the subjects of papers have been maintained during a period of severe economic readjustment is extremely gratifying. This has been made possible very largely by the good work of the Papers and Publications Committee under the able leadership of Mr. J. L. Christie. The decided reduction in funds available for papers and publications has made it necessary to limit the size of the volume; consequently, several of the papers are included in abstract form only.

The Data Sheet Committee, headed by Mr. R. S. Archer, has continued its excellent work of former years. As a direct result the third and latest revision of the National Metals Handbook, which has been offered to Institute of Metals Division members at a pre-publication price of $2.50, and which will be issued in 1933, will contain 400 pages of data devoted to nonferrous metals. The continued cooperation of the American Society for Steel Treating and the Institute of Metals Division in the matter of data is commendable.

With the approval of the Executive Committee, a Committee on Award has been appointed, consisting of R. F. Mehl, *Chairman;* W. M. Peirce and H. A. Bedworth. It shall be among other things the duty of this committee to make available a suitable certificate to be presented each year to the Division's annual (February) lecturer.

The continued participation of the membership in the activities of the Institute of Metals Division is proof of the Institute's great value.

T. S. Fuller, *Chairman,*
Institute of Metals Division.

By-laws of the Institute of Metals Division

[As Adopted February 30, 1930.]

Article I—Name and Object

Sec. 1. This Division shall be known as the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers.

Sec. 2. The object of the Division shall be to furnish a medium of cooperation between those interested in the metallurgy, fabrication and uses of the nonferrous metals and their alloys; to represent the A. I. M. E. in so far as nonferrous metallurgy is concerned, within the rights given in A. I. M. E. By-law XI., Sec. 1, and not inconsistent with the Constitution and By-laws of the A. I. M. E.; to hold meetings for social intercourse and the discussion of nonferrous metallurgy; to stimulate the writing, presentation and discussion of papers of high quality on nonferrous metallurgy; to reject or accept such papers for presentation before meetings of the Division.

Article II—Members

Sec. 1. Any Member, Associate, or Junior Associate of the A. I. M. E. in good standing may become a Member, Associate or Junior Associate of this Division upon registering in writing a desire so to do, but without additional dues.

Sec. 2. But no one who has been continuously indebted to the A. I. M. E. or to this Division for more than three months shall be entitled to vote or to receive publications to which, as a member of the Division, he would be entitled.

Article III—Funds

Sec. 1. The expenditure of the funds received by the Division shall be authorized by the Executive Committee of the Division.

Article IV—Meetings

Sec. 1. The Division shall meet at the same time and place as the annual meeting of the A. I. M. E., and at such other times and places as may be determined by the Executive Committee subject to the approval of the Board of Directors of the A. I. M. E.

Sec. 2. The annual business meeting for election of officers shall be held within a few days before or after the annual business meeting of the A. I. M. E.

Sec. 3. At any meeting of the Division for which notice has been sent to the members of the Division through the regular mail at least one month in advance, a business meeting may be convened by order of the Executive Committee, and any routine business transacted not inconsistent with these By-laws or with the Constitution or By-laws of the A. I. M. E.

Sec. 4. For the transaction of business, the presence of a quorum of not less than 25 members of the Division shall be necessary.

Article V—Officers and Government

Sec. 1. The officers of the Division shall consist of a Chairman, two Vice-chairmen, Secretary and Treasurer. The office of Secretary and Treasurer may be combined in one person, if desired by the Executive Committee.

Sec. 2. The government of the affairs of the Division shall rest in an Executive Committee, in so far as is consistent with the By-laws of the Division and the Constitution and By-laws of the A. I. M. E.

Sec. 3. The Executive Committee shall consist of the Chairmen, two Vice-chairmen, Past-chairman, Secretary, and nine members, all of whom shall be nominated and elected as provided hereafter in Article VII.

Sec. 4. The Chairman and Vice-chairman shall serve for one year each, or until their successors are elected. Each member of the Executive Committee (subsequent to the initial Executive Committee) shall serve three years. The Chairman shall remain a voting member of the Executive Committee for one year after his term as Chairman.

Sec. 5. The Treasurer of the Division shall be invited to meet with the Executive Committee, but without ex-officio right to vote. He shall be appointed annually by the Executive Committee, from the membership of the Executive Committee or otherwise.

Article VI—Committees

Sec. 1. There shall be six standing committees as follows: Papers Committee, Finance Committee, Data Sheet Committee, Membership Committee, Annual Lecture Committee and Research Committee, and such other committees as the Executive Committee may authorize.

Sec. 2. It shall be the duty of the Papers Committee to secure the presentation of papers of appropriate character at meetings of the Division and of the A. I. M. E.

Sec. 3. It shall be the duty of the Finance Committee to inquire into and examine the financial condition of the Division and to consider proper means of increasing its revenue and limiting its expenses.

The Finance Committee shall audit the accounts of the Division and report to the Executive Committee prior to the annual meeting of the Division.

It shall render a budget to the Executive Committee estimating receipts and expenses for the ensuing year so that action can be taken on same at the first meeting following the annual meeting.

Sec. 4. It shall be the duty of the Membership Committee to encourage and solicit membership in the A. I. M. E. and in the Division in accordance with the By-laws and Constitution of the A. I. M. E.

Sec. 5. It shall be the duty of the Annual Lecture Committee to arrange for the presentation at the time of the Annual Meeting of the A. I. M. E. of a lecture on a technical subject of particular interest to the Division and the A. I. M. E. as a whole. This lecture is to be known as the "Institute of Metals Lecture." This Committee shall make all arrangements, financial and otherwise, and render a complete report on same to the Executive Committee.

Sec. 6. The Chairman of the Division shall, subject to approval of the Executive Committee, appoint the Chairman and new members as required of the Committees referred to in Sec. 1.

Sec. 7. Appointments on standing committees shall be for terms of three years each with approximately one-third of the committee membership being appointed each year.

Article VII—Nominations and Elections of Officers and Committees

Sec. 1. Every year the Division shall elect a chairman, two vice-chairmen, a secretary and three members of the Executive Committee.

Sec. 2. A nominating committee of five members of the Division shall be appointed by the Chairman of the Division subject to the approval of the Executive Committee immediately after the annual meeting.

Sec. 3. This Committee shall make its report to the Executive Committee at or before the autumn meeting of the Division.

Sec. 4. Any ten members of the Division may submit nominations for one or more offices to the Executive Committee not later than the date of the autumn meeting, and the persons so nominated shall be included in the official ballot.

Sec. 5. The voting shall be by letter ballot.

Sec. 6. The ballots shall be counted by a committee of tellers appointed by the Executive Committee.

Article VIII—Amendments

Sec. 1. Proposals to amend these By-laws shall be made in writing to the Executive Committee and signed by at least ten members. They shall be considered by the Executive Committee and announced to the members through the columns of *Mining and Metallurgy*, together with any comments or amendments made by the Executive Committee thereon. They shall be voted upon at the annual meeting of the Division in February or by letter ballot, as may be directed by the Executive Committee.

The Institute of Metals Lecture

An annual lectureship was established in 1921 by the Institute of Metals Division, which has come to be one of the important functions of the Annual Meeting of the Institute. A number of distinguished men from this country and abroad have served in this lectureship. The roll is quoted below:

1922 Colloid Chemistry and Metallurgy. By Wilder D. Bancroft.
1923 Solid Solution. By Walter Rosenhain.
1924 The Trend in the Science of Metals. By Zay Jeffries.
1925 Action of Hot Wall: a Factor of Fundamental Influence on the Rapid Corrosion of Water Tubes and Related to the Segregation in Hot Metals. By Carl Benedicks.
1926 The Relation between Metallurgy and Atomic Structure. By Paul D. Foote.
1927 Growth of Metallic Crystals. By Cecil H. Desch.
1928 Twinning in Metals. By C. H. Mathewson.
1929 The Passivity of Metals, and Its Relation to Problems of Corrosion. By Ulick R. Evans.
1930 Hard Metal Carbides and Cemented Tungsten Carbide. By S. L. Hoyt.
1931 X-ray Determination of Alloy Equilibrium Diagrams. By Arne Westgren.
1932 The Age-hardening of Metals. By Paul D. Merica.
1933 Present-day Problems in Theoretical Metallurgy. By Georg Masing.

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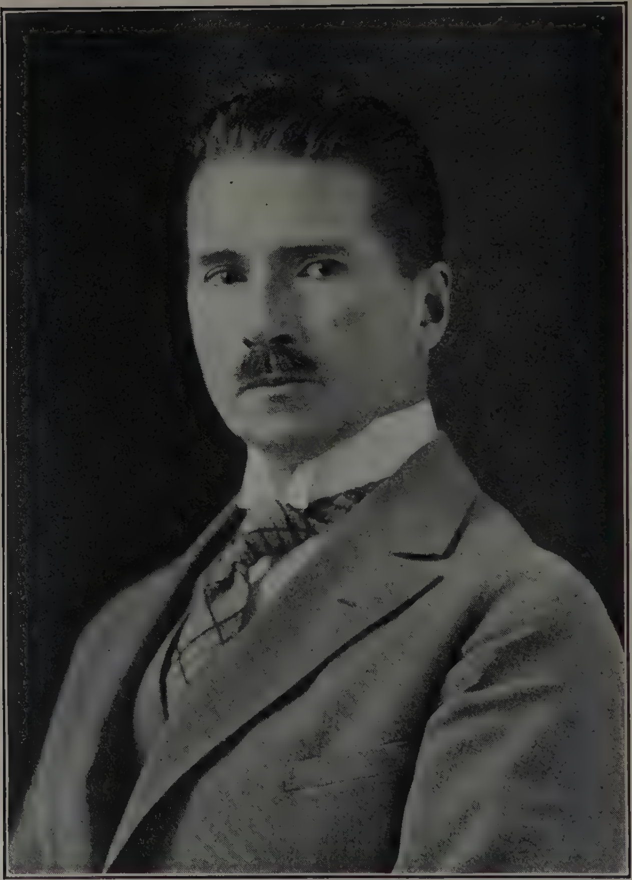
[1] Until February, 1934. [2] Until February, 1935. [3] Until February, 1936.



GEORG MASING

Institute of Metals Division Lecturer, 1933

Present-day Problems of Metallurgy

GEORG MASING,* BERLIN, GERMANY

(Institute of Metals Division Lecture)†

WHILE reflecting on the subject of my present paper, I soon realized that it would be very difficult to say something really new about any special aspects of metallurgy. In consideration of the excellent scientific work that has been done in the United States in connection with almost all the fundamental questions that are of interest today, and of the remarkable abstracts delivered before this Institute and elsewhere in America, I am fully aware that I run the great risk of annoying you by a detailed account on a single problem. I have therefore preferred another method. It is not my task to *teach* you something, as there is no doubt that you are as familiar with the problems involved in physical metallurgy as I am, or even more so, but I would rather *discuss* the matter with you. I trust that this discussion will be useful for both you and me, and I hope, that it will be very instructive for myself.

Before beginning the discussion, it may be well to explain the sense in which the term "physical metallurgy" will be employed in my lecture. On the one hand, metallurgy is understood to be the art of gaining metals from their ores by reducing them from their nonmetallic compounds. This domain may be called "chemical metallurgy." On the other hand, it deals with all the methods of treating metals, once they have been obtained in the metallic state, and with all the properties of metallic systems. In other words, it covers the whole science of metals from the standpoint of their internal structure. The structure is here understood in the widest sense of the word and refers to the atomic arrangement as well as to the macrostructures of a metal. This domain of metallurgy may be called "physical metallurgy." If I am not mistaken, this terminology has been suggested by Dr. Rosenhain.

We shall deal only with the theoretical views of physical metallurgy and not with its practical applications.

In comparing the problems of physical metallurgy of 20 years ago and those of today, we notice a typical change. Physical metallurgy 20 years ago was almost entirely understood to be the doctrine of the constitution of alloys. The investigation of constitutional diagrams was almost the sole problem dealt with in metallography. In other words, the problem was to define the crystal phases of an alloy system, their stability ranges and their composition.

---

* Chief Research Metallurgist, Siemens Concern; President, Deutsche Gesellschaft für Metallkunde.

† Presented at the New York Meeting, February, 1933. Twelfth annual lecture.

The formal laws of heterogeneous equilibrium constitute the basis of the constitutional diagram. This thermodynamic basis has two peculiarities. First, it does not deal with any atomic problems. Its statements are restricted to the number and compositions of thermodynamic phases that are in equilibrium. This restriction, as given by the great American physicist J. Willard Gibbs, has been very useful, because it has enabled the scientist to study heterogeneous equilibria without using the calculations of homogeneous equilibria, which previously had been tried in vain. And, second, it neglects the influence of the surface and of the shape of phases that must be taken into account in the full statement of equilibrium conditions. We know, for example, that the vapor pressure of a liquid depends upon its radius of curvature. Only by neglecting this dependence and assuming that the surfaces are almost plane does one obtain the phase rule, which states that at a given temperature a liquid has a determined vapor pressure. The particles seen in the microscope are, from the atomistic point of view, in general so large as to enable the phase rule practically to be applied to the study of the constitutional diagrams. This law was the reliable guide, without which important progress in the physical metallurgy of 20 or 30 years ago would have been impossible.

But today the most interesting problems of physical metallurgy are of atomic character. In this respect, physical metallurgy has a share in the development of the other physical sciences. You are well aware that physics plays a leading part in the natural sciences of today. These sciences increasingly employ almost all physical methods of investigation, and the limiting line between them and pure physics can often hardly be discovered. It is the increasing application of X-ray analysis, that has mostly caused this development.

This change from formal thermodynamics to the atomic theory has taken place gradually. The plasticity of metals was perhaps the chief problem subject to such development. It was rather thoroughly investigated by Ewing and Rosenhain[1] as early as in 1900, but in Germany it did not become an essential problem of physical metallurgy until a decade later (1912) following the research work done by Heyn[2] and by Tammann.[3] The plasticity of metals is connected with the important problem of the crystallographic slip, and this is naturally an atomic problem. Unfortunately, this problem is so difficult that the atomic mechanism of the slipping process is at present almost as obscure as it was 20 years ago. It is obvious, of course, that formal thermodynamics, or the phase rule, cannot help us here.

---

[1] Ewing and W. Rosenhain: *Phil. Trans.* Roy. Soc. (1900) **136A,** 353.

[2] E. Heyn and Martens: Handbuch d. Materialienkd. 1912.

[3] G. Tammann: Lehrbuch d. Metallkunde. 1914.

Another important problem was initiated by Tammann[4] at the beginning of the World War. He stated that certain alloys which give an uninterrupted series of mixed crystals, as for example the silver-gold alloys, are not attacked at all by a reagent dissolving the less noble metal, provided the concentration of this metal is less than 25 or 50 atomic per cent (according to the nature of the reagent), but that the amount of this metal dissolved in such reagents rises quickly and reaches 100 per cent as soon as this concentration is exceeded. This means, for example, that from the alloys of silver with gold that contain more than 50 atomic per cent of silver almost all the silver is dissolved in the nitric acid, whereas the gold remains unattacked. Tammann called the concentration at which the less noble metal begins to be dissolved the parting limit.

The most unexpected discovery of such parting limits and of the protecting power of the noble metals in their alloys greatly affected the question of the atomic arrangement in mixed crystals. This atomic problem was first investigated by chemical means and by statistical calculations and later with the aid of X-rays. We shall study it more closely in the following discussion.

Actually, the constitution of alloys is still one of the main problems of physical metallurgy, but its meaning is now quite different from what it was before. At present, we regard it as the atomic lattice structure, as investigated, for example, by Westgren, and not merely the structure to be seen in the microscope.

Furthermore the problems of diffusion, of the building and of the development of new crystal kinds in an alloy have been investigated for more than 20 years past. These are typical atomic problems. Age-hardening is one of them, and we shall deal with it later.

This change from the thermodynamic to the atomic standpoint has given physical metallurgy many chances of advance, but has also led to some theoretical difficulties. The human mind is naturally to a certain degree one-sided. Every theory has a positive content of statements and neglects at the same time questions that are of minor interest for this particular theory. These defections are likely to be forgotten, and the theory enlarged until it reaches a point where it cannot stand its ground.

If a new theoretical view is started, which is capable of clearing up questions left more or less obscure by the preceding theory, many difficulties and apparent contradictions arise, which, on the one hand, obstruct the development of the new theory and, on the other hand, tend to abolish even valuable parts of the old theory.

I wish to discuss some of the problems of physical metallurgy from the point of view indicated above; in other words, point out the transition from the doctrine of heterogeneous equilibria to the atomic point of view and the peculiarities and difficulties arising from this transition.

---

[4] G. Tammann: *Ztsch. f. anorg. Chem.* (1919) **107**, 62.

Parting Limits

We begin with the theory of parting limits. The behavior of such alloys as Ag-Au against a reagent such as nitric acid, which attacks only one component of the alloy, has been pointed out above. See Fig. 1.

From the point of view of thermodynamic equilibrium, such a behavior cannot be understood. In the case of equilibrium, a certain value of electrolytic dissolving power corresponds to each concentration of the alloy, and the process of solution of silver in the electrolyte can be counterbalanced only by the osmotic pressure of silver ions in the electrolyte. If the electrolyte contains a certain amount of silver, the concentration of silver in the alloy can never fall to zero, as has been found after short times of reaction with the nitric acid when the alloy contains more than about 62 per cent of silver, and it must gradually be reduced to zero from alloys of all concentrations, if the acid does not contain silver ions. But the fact that the reaction with the acid ceases practically completely as soon as the concentration of silver in the alloy falls below 50 atomic per cent, in other words below the parting limit, cannot be explained with the aid of thermodynamics. Its explanation is only possible if we assume that inner diffusion of the alloy, as a state of a movable equilibrium, does not exist at the temperature concerned and that the arrangement of the atoms in the crystal lattice is such that the atoms of gold protect the atoms of silver from the reaction with the acid.

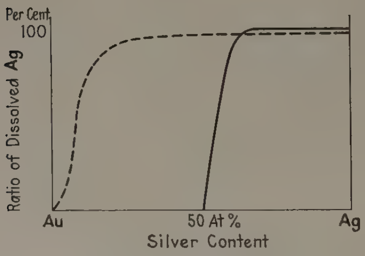


Fig. 1.—Parting limits in gold-silver alloys.

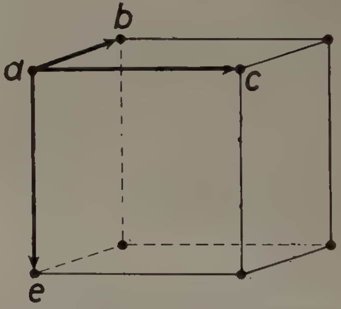


Fig. 2.—Coordination number of a simple cubic lattice.

For reagents that are weaker and mostly bivalent, the parting limit lies at 25 atomic per cent. (Later we shall see that this assertion is only approximately correct.)

How can an atomic arrangement explain the existence of parting limits at 25 and at 50 atomic per cent? Before answering this question, one must have a conception of the path enabling the reagent to penetrate into the inner part of the metal.

Let us consider a simple cubic lattice, Fig. 2. The shortest distances between atoms are along the borders of the elementary cell. For every atom *a*, there are six atoms surrounding it at the shortest distance *d*; namely, the atoms *b*, *c* and *e* in the primitive cell represented in the figure and three others in the neighboring cells. G. Tammann[5] has supposed that the reagent can proceed only from one nonresistant atom to another, the shortest distance away, and that an atom *a* is protected from the action of the reagent if no atoms in the immediate neighborhood are attacked by the reagent, because they are noble or because they are protected in one way or another.

The solution of the reactive atoms is therefore considered to proceed from the surface along "coherent paths" of reactive atoms, in which two neighboring atoms are spaced at the shortest possible distance in the space lattice concerned.

Tammann[6] has tried to calculate the resistance of an alloy by means of a statistical method, under the assumption that the atoms of both metals in the lattice are distributed at random. Let the atomic concentration of the reactive atoms be p, and of the noble atoms q. ($p + q = 1$) Consider the reactive atom *a*, Fig. 2. Evidently it will be protected, if it is surrounded by six nonreactive atoms. For this purpose, there must be a group of seven atoms in the arrangement indicated in Fig. 2. The probability of such a group is in accordance with the theory of probabilities: $7qp^6$, if it is assumed that the reactive atom p may have any given position; viz., in the middle of the group, as well as at one of the other points. From these seven positions it would be protected only in the first. The probability of such a protective group is therefore only one-seventh of that mentioned above, therefore simply: $p \cdot q^6$.

There are still other protecting groups containing two or more reactive atoms. To be protected, these atoms must be surrounded by more than six nonreactive atoms. Therefore it becomes necessary to consider groups containing much more than seven atoms. The more atoms a group contains, the less is its probability value.

All the larger groups together give much smaller probability values than does the group having seven atoms. By adding all these probability expressions, Tammann obtained the probability of protection of the reactive atoms in dependence on the atomic ratio. If the numbers of the atoms considered are, as practically in every crystal, very large, this probability number gives the ratio of protected reactive atoms in the whole crystal. In this way he obtained the dotted curve in Fig. 1 as against the straight line found experimentally.

This contradiction between the calculated and the experimental results has led Tammann to the conclusion that the basis of the calcula-

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[5,6] Reference of footnote 4.

tion was erroneous; in other words, that the atoms in a mixed crystal must be arranged in a *regular* manner (symmetrically).

Tammann has calculated the possible regular arrangements in different crystal lattices at different concentrations and has pointed out that the parting limit is likely to lie preferably at 25 or 50 atomic per cent of the components. It is not necessary for us to elaborate these ideas, because it has been proved since by means of X-ray investigation that the atoms are distributed at random in the alloys of copper and gold, if fairly quickly cooled. Let us consider a face-centered cubic lattice and let us assume that the regular arrangement of atoms is such that the atoms of gold lie in the corners, whereas all atoms entering the faces of the unit cube are of copper (Fig. 3). This corresponds to 25 atomic per cent of gold. In this case, we should expect on the X-ray Debye film the so-called "superstructure" lines corresponding to the identity period *d*, this signifying the shortest distance from point to point at which the atomic arrangement is repeated, as against *one-half* the identity period in the random arrangement of the atoms.

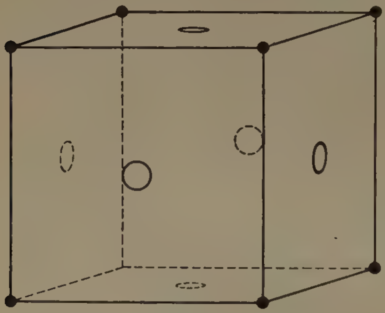

FIG. 3.

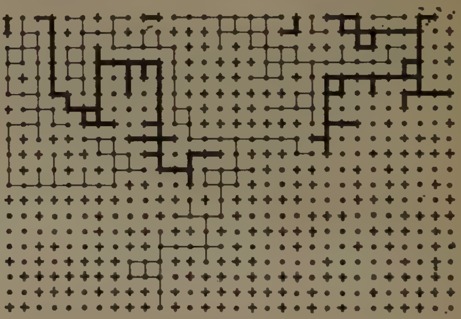

FIG. 4.

FIG. 3.—FACE-CENTERED LATTICE WITH 25 PER CENT GOLD, REGULAR DISTRIBUTION OF ATOMS.

FIG. 4.—PLAIN LATTICE WITH RANDOM DISTRIBUTION OF COMPONENTS.

No superstructure lines have been found in the alloys of silver with gold. In the alloys of copper with gold, the superstructure lines appear only after tempering below the transition points at 400°, but the parting limit is developed with alloys not treated in this way. Thus it is clearly proved that no connection exists between the parting limits and the regular arrangement of atoms in the lattice.

But how can the existence of parting limits and their position at definite concentration points then be explained, since the statistical calculation of Tammann has led to quite a false result?

This calculation is incomplete. Consider the two dimensional lattice models in Fig. 4.

Let the points be the noble atoms and the crosses the reactive ones. Their arrangement is an irregular one. Let us now consider the coherent paths of reactive atoms from the upper end of the lattice. If the reaction proceeds along these paths, only such atoms as lie there will be attacked by the reagent; all the other reactive atoms will be protected. Now there are large areas into which the reagent does not penetrate at all, regardless of the position of single atoms in these parts as Tammann conceived it.

Apart from the protected positions of reactive atoms envisaged by Tammann, there are conditions that enable entire *blocks* of crystals to be protected. These conditions were neglected by Tammann.

How can the probability of such protective conditions be calculated? I have tried to do this in the following way:[7,8]

The principles underlying such a calculation may be seen from a plane model lattice, Fig. 5, which is the lattice shown in Fig. 4, but turned through an angle of 45°. Let us suppose that the attack is proceeding from the upper end along coherent paths, and let us introduce one restriction. The attack can proceed from the upper to the lower part, but cannot be reversed. In other words, paths such as the one indicated in Fig. 5 on the left are possible, but paths similar to the one on the right are not possible. This is, of course, quite an artificial restriction, but it simplifies the discussion to a large extent and has for this reason been introduced by Borelius.[9]

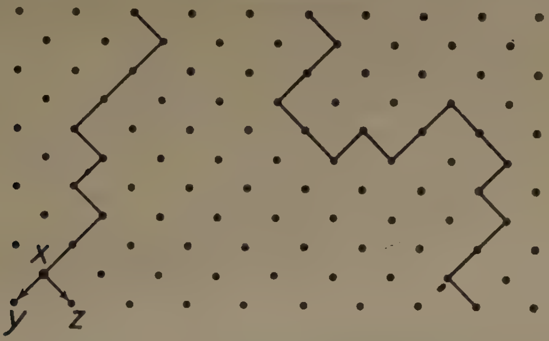

Fig. 5.—Calculation of coherent paths.

We consider a great number of the paths as in Fig. 5 during the step-by-step progression of the attack of the reagent into the inner part of the lattice. We try to calculate the chance of the reactive atoms being reached by the reagent progressing in this way. If the reagent has reached the point x, it can proceed further in two directions, to y and to z. If both are reactive atoms, the number of the atoms attacked by the reagent at the steps corresponding to y and z will be greater than at the step x. If both atoms are resistive, the path will be abruptly terminated

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[7] G. Masing: *Ztsch. f. anorg. Chem.* (1921) **118**, 293.

[8] G. Masing: *Wiss. Veröffentl.* a.d. Siemenskonzern (1926) **5**, 156.

[9] G. Borelius: *Ann. d. Phys.* (1924) **74**, 216.

at x. We consider the mean ratio of the number of reactive atoms reached by the reagent at the step y, z to the same number at the step x, for a great number of paths such as the left in Fig. 5. If this ratio is less than unity, the coherent paths will die away one after the other, the reagent will be capable only of penetrating into the superficial layer of the lattice and the body will be resistant. If this ratio is greater than unity, the paths will be gradually increased by the developing of new branches and the reagent will penetrate into the whole alloy.

The parting limit lies obviously at the concentration point where this ratio is equal to 1.

The probability that at the point y or at the point z there will be a reactive atom is simply p, if p is the atomic concentration of this atom in the lattice under consideration. The required ratio R will then be $R = 2p$, or the parting limit = 0.5 = 50 per cent, in agreement with experiment. Nevertheless this result is erroneous. We have deduced it by assuming that, at least in the neighborhood of the parting limit, the different paths will be sufficiently remote one from the other to avoid mutual interference. In other words, we suppose that the reactive elements actually *reached* by the reagent are distributed statistically over every step of the path under consideration. But this is not so. The distribution at the step y, z is, for example, not independent of the distribution at the foregoing step.

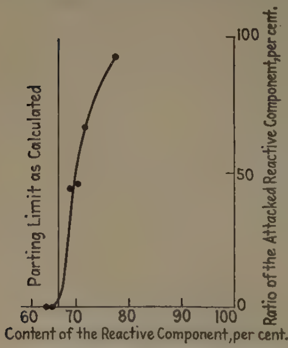

FIG. 6.—PARTING LIMIT IN A PLAIN MODEL AS FOUND BY ENUMERATION.

Therefore it cannot be calculated statistically, and it is possible—and proves to be so—that different coherent paths interfere with one another even in the neighborhood of the parting limit.

Borelius has calculated the parting limit in a somewhat different way. But since he also assumes a regular distribution of the attacked atoms in the inner part of the lattice, he obtains the same false result that I do.

By a simple construction of coherent paths on a model lattice, Fig. 5, and by counting the attacked atoms, we obtain a parting limit a little above 66 atomic per cent of the resistant component, as I have shown above. Fig. 6 shows the ratio of the attacked atoms at different concentration points.

I have tried to avoid this fault by a modified calculation. This becomes very troublesome but I have succeeded in calculating the parting limit approximately between the atomic ratios 0.651 and 0.67 of the noble component, which is in close agreement with the result of the experiment by graphic enumeration. It has therefore been proved with the help of the model that there are marked parting limits, even when the atoms are distributed at random. This result is very likely to hold for three-dimensional lattices. There now remains the discussion of the concentration at the parting limit.

I have already mentioned that it seems to be almost impossible exactly to calculate this limit in a real crystal.

But there appears to be another possibility of dealing with the problem, as has been shown by Borelius.[10] In a plane lattice like that of Fig. 4, the condition of corrosion resistance of the alloy is that the coherent paths of the reactive atoms terminate in the neighborhood of the surface. But this means that they must be surrounded by coherent chains of resistant atoms. The condition of resistivity is then the existence of coherent paths of resistant atoms and the condition of reactivity of the alloy, the existence of similar paths of active atoms. Therefore the parting limit can lie only at the atomic ratio 1:1; thus at 50 atomic per cent Borelius has been able to find this parting limit by counting the reactive atoms reached by the reagent on a plane model as that of Fig. 4; all the directions of closely spaced steps being admissible. Collaterally, this result proves directly that Tammann's statistical calculation, as indicated above, is not correct. He has, indeed, computed his curve, given in Fig. 1, for four protecting atoms, as shown in the plane lattice Fig. 4. Thus the curve is in strict contradiction with the result obtained by Borelius from his enumeration method.

If we desire to apply these considerations of symmetry to three-dimensional crystals, we must operate with *inner surfaces* instead of *chains* of atoms. Hence we shall say that the action of the reagent depends on the existence of coherent inner surfaces consisting only of the one or the other kind of atoms. If the crystal is reactive, it is divided by coherent surfaces of reactive atoms into a great number of parts. It is, on the contrary, resistant if these coherent surfaces consist of resistant atoms. The two conditions exclude one another, and the parting limit must be again at 50 atomic per cent.

At first sight it seems to be very improbable that coherent surfaces should be decisive for reactivity or chemical resistance. A closer consideration shows, however, that the fundamental condition of *coherent chains* is less probable. The reagent (for example, nitric acid) has a molecular volume that is larger than that of the single atoms in the space lattice. This reagent therefore will not be able to proceed along such small paths as define the chains of reactive atoms. Furthermore, the products of the reaction, the metal cations and the lower nitric oxides, must be removed before the reaction can proceed further, and must be driven into aqueous solution. A far larger space is thus required for the continuous reaction than for that given in a *chain* of reactive atoms, and the assumption of such chains must be regarded merely as a fictitious image of the facts.

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[10] G. Borelius: Reference of footnote 9.

It may be assumed—and we shall enter later more fully into this question—that the reaction proceeding from the outer surface of the metallic body destroys it in some way, until it finds a barrier in a surface consisting only of noble atoms.

In this way it seems not impossible to understand that the parting limit must lie at 50 atomic per cent. But the explanation is still highly hypothetical and can be considered satisfactory only if it enables other facts to be predicted without using some new and difficult hypothesis.

We may now consider the second parting limit, which, according to Tammann, lies at 75 atomic per cent of the reactive component. Tammann has observed that this parting limit is found, if the reagent is *bivalent,* in the case of the ordinary 50 atomic per cent limit. Even this assertion may be considered to be indistinct; it is an established fact that the 50 per cent parting limit occurs in highly reactive electrolytes, while the 25 per cent parting limit is found in less reactive electrolytes. In the case of the 50 per cent limit the condition of the limit can be supposed to be symmetrical, so far as the single points of the lattice are concerned. They must be occupied as often by the atoms of the one as by those of the other component. The probabilities for these two events are simply given by the atomic ratios p and q for the reactive atoms P and the resistive atoms Q, respectively, and the required condition is $p = q$, or $p = q = 0.5$, since $p + q = 1$.

We may suppose that in the case of a bivalent or a less energetic reagent the groups containing one single atom are no longer decisive, but rather the groups set up of *two atoms.* This supposition is not quite new; Tammann has already employed it, in discussing parting limits on the basis of regular atomic arrangements. We shall suppose, furthermore, as Tammann did, that in such a case a group of two atoms is reactive only when it consists of two reactive atoms. If it consists of one reactive and one resistant atom, it is resistant as a whole.

The condition of the parting limit will again be that the probability of the resistant two-atomic groups is equal to the probability of the reactive groups.

The probability of the groups consisting of two reactive atoms is p^2, of the two resistant atoms q^2, and of a resistant and a reactive atom $2pq$. (The sum of these probabilities must be 1.) The parting limit is therefore given by the equation

$$p^2 = 2pq + q^2 = 1 - p^2$$

or

$$p = \frac{1}{\sqrt{2}} = 0.71 \text{ and } q = 0.29$$

instead of 0.75 for the reactive component, or 0.25 for the resistant component, as given by Tammann.

Table 1 shows some values of parting limits given by Tammann for the alloy of gold with silver and of gold with copper, which have been investigated most thoroughly.

TABLE 1.—*Parting Limits as Found by G. Tammann*

Reagent	Au-concentration, Atomic Per Cent	
	Cu-Au	Ag-Au
$PdCl_2$	0.245–0.255	
$Pd(NO_3)_2$		0.245–0.255
$PtCl_2$	0.245–0.255	0.245–0.255
$(NH_4)_2S_2$	0.245–0.255	>0.32
Na_2S_2		0.27 –0.32
$S\ Cl_2$	0.22	
Na_2S	0.22	0.27
Pure acid	0.22	
Na_2Se_2	0.245–0.255	>0.27
$AuCl_3$		0.495–0.505
H_2CrO_4		0.492
$M\ MnO_4$		0.495–0.505
HNO_3		0.480–0.490

The 0.25 limit is fairly well indicated in the case of some reagents with copper-gold alloys and, to some extent, with silver-gold alloys; but generally this parting limit tends to lie in the former, below and, in the latter, above this figure for the concentration of the noble component. In general, this limit is less defined and fluctuates more than the 50 atomic per cent limit. In the silver-gold alloys, the former limit is poorly defined.

Table 1 shows that the parting limit of the silver-gold alloys lies often in the neighborhood of 0.29, as required by the calculation. The mean value as given in Table 1 of the limit for these alloys is about 0.276. The mean value for the alloys of copper and gold, about 0.233, is lower by 0.04 than for the silver-gold alloys. This deduction of 0.25 parting has been given by Dehlinger and Glocker.[11]

Now, from the theoretical point of view, one is justified in expecting that the silver-gold alloys are more ideal solid solutions than are the gold-copper alloys, since the latter form the compounds Cu_3Au and $CuAu$. Therefore it may be supposed that at higher temperature (above the temperature of the formation of these compounds) the affinity between copper and gold acts according to the law of the distribution of atoms in the space lattice. Let us suppose that owing to this affinity groups of two atoms of gold cannot exist in these alloys. Let us, moreover, consider a portion of the space lattice having N (a large number) of atoms, and let p and q be the ratios of the copper and gold atoms respectively with each atom surrounded by n atoms at the shortest distance (coordination number). Then the number of all groups of two atoms will be

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[11] U. Dehlinger and R. Glocker: *Ztsch. f. Phys.*

$$\frac{n \cdot N}{2}$$

The number of gold atoms is Nq and the number of groups in which the gold participates,

$$Nqn$$

All the other groups consist of copper atoms only; their number is:

$$\frac{n \cdot N}{2} - Nqn$$

These are reactive.

The parting limit is given by the relation

$$Nqn = \frac{nN}{2} - Nqn$$

or

$$q = \tfrac{1}{4} - 0.25$$

In this case, the parting limit is lowered by about 0.04 as compared with that of the silver-gold alloys.

We shall not discuss the question of the copper-gold alloys here in detail, because we stand at the moment upon highly uncertain ground. It may be mentioned, however, that if the difference between the gold-silver and the gold-copper alloys with respect to parting limits depends on deviations of the latter alloys from a simple random distribution of the single atoms in the space lattice, it should be expected that the law of the distribution of single atoms must be different at different temperatures above the temperature of formation of the compound $AuCu_3$, which is stable only beyond about 400° C. By quenching these alloys from different temperatures and by determining their parting limits, it must therefore be possible to ascertain these changes in the law of distribution of the atoms.

Generally speaking, it is today of little value to set up any imaginary mechanism of reaction for explaining the actually observed position of the parting limits. Real advance can be made only on the basis of experimental investigation of the mechanism itself. The sole successful attempt in this direction has been made by Graf,[12] who has investigated the reactions of different gold-copper alloys with the help of X-ray observations. He has found that the nitric acid in which the parting limit lies at 50 atomic per cent, when reacting with alloys poorer in gold than this figure, converts the space lattice into one of pure gold. The diffraction lines of gold are well defined and the orientation of the gold crystals is the same as that of the unattacked alloy. If the alloy is attacked by a concentrated nitric acid, the diffraction lines are broadened equally on both sides of the true copper value. They show in part new orientations of crystals, as, in addition to the black spots corresponding to the prior orientation, fainter continuous ranges of Debye lines may be seen.

The same effect is observed, if the alloy is treated with a mixture of nitric and hydrochloric acid, this mixture dissolving, as is known, not only copper but also gold.

By carefully etching off the surface layer of gold, Graf has been able to show that there is no gradual change of lattice constant between the unattacked alloy and the gold—evidently the latter is located upon the unaltered alloy and intermediate concentrations do not occur between the two bodies.

From these observations, Graf concludes that nitric acid is capable of bringing gold into the ionic state, but only at the weak points of the space lattice; for example, at the corners left after the solution of copper atoms. Perhaps the gold atoms are also in the ionic state on the entire surface of the alloy, with this one atomic layer held adsorbed by the underlying space lattice. Only the atoms at the "weak" points can travel in the electrolyte. But surely the degree of mobility will be higher for an ionized surface than for the atoms in the space lattice.

It may be assumed that the gold ions cannot be stable in the presence of metallic copper atoms. The copper atoms must be ionized while the gold ions are being reduced by the copper. From a general point of view, this is an *electrolytic* reduction of gold.

Consider the plane lattice Fig. 7*A*, the crosses being the copper atoms and the points the gold atoms. The upper part of the figure is assumed to be the surface at which the reaction starts. In the next moment, the atoms of copper will be dissolved in the acid and also the gold atoms 1 and 2 occupying weak positions, while the other gold atoms will be ionized. Representing the gold ions by circles, we thus obtain Fig. 7*B*. The copper atom will be oxidized by one of the two gold cations located above it, the other will be dissolved, as being now in a "weak" position. The gold atoms of the surface will again be ionized, the copper atoms will be dissolved and, as the next step of the reaction, we shall obtain Fig. 7*C*. By adding identical steps we shall obtain Figs. *D* and *E*.

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[12] L. Graf: *Ztsch. f. Metallkunde* (1932) **24,** 248.

In this way we have obtained an impression of the reaction process which differs widely from that of the "coherent paths" discussed above. The position of the parting limit to which this reaction mechanism may lead has not yet been calculated; but it is not impossible that it may lead to the condition of Borelius, which means that the reaction will be finished as soon as a coherent surface of resistive atoms is reached. U. Dehlinger and R. Glocker (*Op. cit.*) calculate the parting limit on the basis of the results of Graf in a somewhat different way. They assume that the gold atoms of the surface are movable in the sense of M. Volmer and W. Weber but are not ionized. Their mobility enables them to fill up voids left by dissolution of copper atoms; thus leading to the formation of a coherent protective layer of gold atoms. This conception uses also the results of Graf and signifies therefore a progress as compared with the former calculations. It is impossible to decide today whether the conception of Graf or that of Dehlinger and Glocker corresponds more closely to the truth. But Graf's observations of the diffraction lines of the space lattice of gold after the action of the nitric acid are sharp in the same way as in the case of the action of nitric and hydrochloric acid together, which makes the view of Graf more probable.

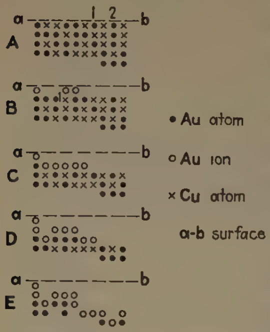

FIG. 7.—SCHEMATIC ARRANGEMENT SHOWING REACTION OF COPPER-GOLD LATTICE WITH HNO_3.

As to the reaction with reagents that shows the parting limit at 25 per cent of the nobler component, Graf has found that by treating alloys containing 10 to 15 atomic per cent gold no space lattice of pure gold is formed. But the diffraction areas of the outer surface were broadened after the reaction had ceased, and from this broadening it has been calculated that the gold content of the surface layer may vary from 20 to 40 atomic per cent. Graf's conception is that the less reactive electrolytes having a parting limit at 25 atomic per cent do not involve a transition of the gold atoms into the ionized state, but that the single gold atoms lying at the "weak" points of the surface after solution of the copper atoms are, to a certain degree, still movable, although less so than when in the state of cations. They may travel on the surface, therefore, until they fall to deeper levels and are fixed there. In this way, we may obtain broken off crystal pieces with coherent gold surface layers and various copper contents.

The question as to the mechanism of reaction producing in this case a parting limit in the neighborhood of 25 per cent is not yet settled. But it is noteworthy that although the reaction residue is pure gold with strong reagents such as nitric acid, as previously known, this is not so with the milder reagent having the lower parting limit. This is an entirely new condition, which had not been expected from the point of view of Tammann's theory. The assumption of a solution along "coherent paths" of atoms cannot explain it.

In order to make a more definite statement as to these conditions, it will be necessary to investigate the matter more thoroughly in an experimental manner.

AGING

Age-hardening is one of the most important problems faced in present-day metallurgy both from the practical and the theoretical standpoint. Dr. Merica[13] dealt with this problem in his lecture last year, and I am glad to say that I find myself in agreement with him at almost every point. Therefore I shall not discuss the technical questions of age-hardening but rather confine myself to a consideration of three or four theoretical questions, that seem to me most interesting today.

You are well aware that an alloy can only be age-hardened if it is obtainable at ordinary temperature in the state of a supersaturated solution. This holds for the alloy of Fig. 8, which is homogeneous at temperatures above t_2 and is obtainable at room temperature t_0 in the homogeneous state when quenched from the former temperature. If we raise its temperature after quenching to an intermediate value t_1 the alloy will be age-hardened; that is, its hardness and strength will be increased and several other properties altered. For some alloys, for example, duralumin, the temperature t_1 coincides with t_0, and they can therefore be aged at ordinary temperature.

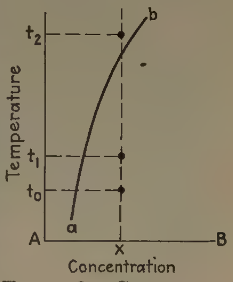

FIG. 8.—SOLUBILITY LINE.

These conditions of the aging process clearly indicate that it is in some way connected with the decomposition of the solid solution. Now, the alloyed metal exists in the mixed crystal in atomic dispersion, and it is coagulated as completed crystals after the excess has been separated from the supersaturated mixed crystal and after the equilibrium has been reached. It is therefore quite evident that the intermediate state of the age-hardened alloy corresponds to some intermediate state of dispersion, or to some degree of "critical dispersion." In this general sense, the "critical dispersion" theory of age-hardening is quite secured today. This is the first basic point I have desired to emphasize.

The second point refers to the question as to the degree of dispersion that is critical. This question has not yet been definitely solved. Surely it has a different aspect for different alloys.

There are alloys in which the hardening is accompanied by striation on the polished surface within individual crystals. The beryllium-copper alloys behave in this manner (Fig. 9). In line with the results of the investigation with the aid of X-rays, which shows broadening of the diffraction lines of the α crystals from the beginning of the age-hardening, it is apparently justifiable to speak in this case of the segregation of a second crystal type and to assume that critical dispersion is understood to mean simply a certain magnitude of the separated γ crystals.

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[13] P. Merica: *Trans.* A.I.M.E. (1932) **99,** 13.

But duralumin and the alloys of aluminum with copper show quite a different behavior. The X-ray intensity analysis shows that the continuous background of the X-ray patterns becomes less darkened during aging as compared with the pattern of the quenched alloy. At the same time the intensity of the Debye diffraction lines rises, especially of those corresponding to the higher indices.[14] These statements are explained by the assumption that the lattice-distorting influence of the diluted copper is lowered by aging. On this basis of X-ray interpretation it is actually taken for granted that in these alloys the age-hardening at ordinary temperatures occurs through accumulation of copper atoms into small groups within the aluminum mixed crystal, this being the first stage of a further separation. In this case the "critical dispersion" corresponds to quite another, obviously much smaller, magnitude of the nuclei and has quite another meaning.

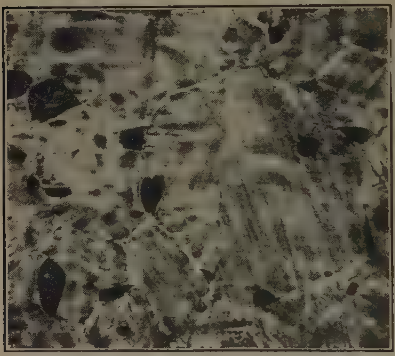

FIG. 9.—BERYLLIUM-COPPER ALLOY (2.5 PER CENT BE) TEMPERED 15 MINUTES AT 350° C. × 230.

Are the groups of copper atoms at this stage to be considered real nuclei of a second crystal type? This seems to be impossible. The lattice constant of the mixed crystal is in fact not altered by the agglomeration of copper atoms into such groups; but even if true copper nucleii groups were very small, such an alteration should be expected, since their separation would mean a change in concentration of the aluminum mixed crystal. To explain the fact that there is no noticeable change of the crystal lattice, it must be assumed that the lattice constant, as measured by means of X-rays, corresponds to a mean value between parts of maxima and minima copper content. Therefore these parts must still be optically coherent. This seems possible only if both remain in the same space lattice.

Here we have to deal with a typical problem involved in present-day metallurgy. As the classical differentiation between different phases fails to explain the phenomena, the possible intermediate states should be borne in mind. Yet it is possible that the question whether a group of copper atoms in the space lattice of an aluminum mixed crystal is a nucleus of a second phase (Al_2Cu) or not is of no account. The formation of the crystals of the compound Al_2Cu from the groups of copper atoms is likely to proceed continuously. These groups will form distortions in the space lattice of the mixed crystal, which will gradually increase with their increasing size, while its inner structure approaches more and more that of the space lattice of $CuAl_2$. From the atomic point of view, the formation of a second phase can be regarded as a continuous process. The formation of $CuAl_2$ has been recently considered in this light by Mehl.[15]

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[14] G. Hengstenberg and G. Wassermann: *Ztsch. f. Metallkunde* (1931) **23**, 114.

The definitions of the classical phase rule become useless in such cases. As to such processes, it is of little use to ask how many phases there are or whether a process is a heterogeneous or homogeneous one. The designations, "phase," "nucleus," etc., fail in their ordinary sense, but this does not mean that they become superfluous or erroneous; they are merely not sufficient to solve the atomic problems under consideration.

But in a wider sense we may still speak of nuclei in the case of copper groups present in duralumin at ordinary temperature. The thermodynamic meaning of the formation of a nucleus is the sudden acquisition of stability. In every solution phase there occur occasionally groups of two or more dissolved atoms in close association. But if the solution is not saturated, such groups will not be stable and will disperse after a very short time into the surrounding solid solution. In a supersaturated solution there will be a certain critical inferior limit of magnitude, above which they become stable. These groups differ from their surroundings and therefore will have a term of free energy corresponding to the free energy of the surfaces in the liquid state. It is this term of free energy that makes these groups unstable if they are very small, and that loses its influence as they increase in size. When these groups reach the "critical range," they will not be dissolved again but will remain in the original state of formation. We must therefore regard them as true "nuclei" in the thermodynamic sense of this word.

For this reason the groups of copper atoms in duralumin, or "knots," as Dr. Merica calls them, are "nuclei," because they are stable. Another question is whether another jump of stability is produced when these groups lose their "optical contact" with the matrix phase and become true crystals of the second phase. We have already considered this question and there is in principle no necessity for this second change.

However, there is another feature that makes it appear probable that there is a material difference between the formation of the "groups" or "knots" of copper atoms in the space lattice of the mixed crystal and the formation and growth of crystals of a second phase. Dr. Merica has directed attention to the fact that the hardness of duralumin, when once reached, has a remarkably high degree of thermal stability. Its loss seems to begin only at temperatures as high as about 200° C. In this connection, duralumin differs appreciably from some other age-hardenable alloys, such as the alloys of beryllium. For these, the hardness begins, in general, to decrease at the same temperature at which its maximum value is reached if the time of aging is unduly prolonged, while duralumin can be held for years at ordinary temperatures before the hardness starts to sink.

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[15] R. F. Mehl, C. S. Barrett and F. N. Rhines: *Trans.* A. I. M. E. (1932) **99**, 226.

This great stability of age-hardened duralumin makes it probable that the "knots" of copper atoms are in some way stabilized so that the diffusion that leads to their formation ceases as soon as they are formed. An explanation for this assumption has recently been given by Dehlinger,[16] who supposes that the knots are formed by only one diffusion step; viz., by one change of place of atoms. As the knot is more stable than the supersaturated mixed crystal, such a diffusion step must be connected with a certain affinity force facilitating the formation of the knot and making its re-solution difficult. This is therefore not a real diffusion, but rather an *irreversible* reaction in the solid state.

By means of a brief calculation, we can show that the formation of knots in such a process is probable even in solid solutions as dilute as duralumin with 5 per cent copper by weight = 2.2 atomic per cent copper. In this alloy about 50 aluminum atoms correspond to one copper atom.

In the face-centered space lattice of aluminum every atom is surrounded by 12 atoms at the shortest distance and by about 48 atoms at double this distance.

It may therefore be roughly assumed that a knot of 3 copper atoms can be formed if a group of about 64 copper atoms contains at least 3 atoms of copper. The probability of such a group of 64 atoms is about 0.15, as follows:

GROUPS OF 64 ATOMS IN AL WITH 2 ATOMIC PER CENT CU

NUMBER OF CU ATOMS	PROBABILITY
1 or more	0.73
2 or more	0.38
3 or more	0.15

It may be supposed that the distance separating the copper atoms in the "knots" is about double that separating the single atoms in the aluminum space lattice.

With relation to the subject of nuclei we shall deal with a *third point* discussed also in Dr. Merica's lecture;[17] that is the fact that an age-hardenable alloy, if aged at a lower temperature and rapidly heated to a higher temperature, first loses to some extent its hardening effect before the hardening again starts at the higher temperature, as may be seen from Fig. 10. This phenomenon seems to occur in very different age-hardenable alloys.

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[16] U. Dehlinger: *Ztsch. f. Phys.* (1932) **79**, 550.

[17] Reference of footnote 13.

We have studied this phenomenon in detail in duralumin, in connection with variations due to changes in the electrical conductivity, and have arrived at the following conclusions:

If during the first aging at low temperatures the conductivity decreases, it rises at once in an accelerated manner after being heated to higher temperatures. In this case, the reduction in hardness involves increased conductivity (Fig. 11). If the conditions at the lower temperature are such that the conductivity after decreasing rises again (in other words, if the initial temperature is higher than as shown in Fig. 11, the conductivity first drops after rapid heating to the second (higher) temperature and then rises again (Fig. 12). The last rise corresponds to the normal behavior of duralumin when treated at this temperature.

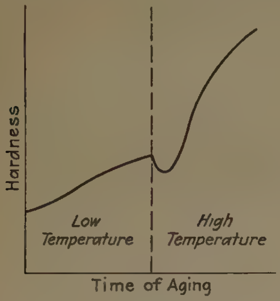

FIG. 10.

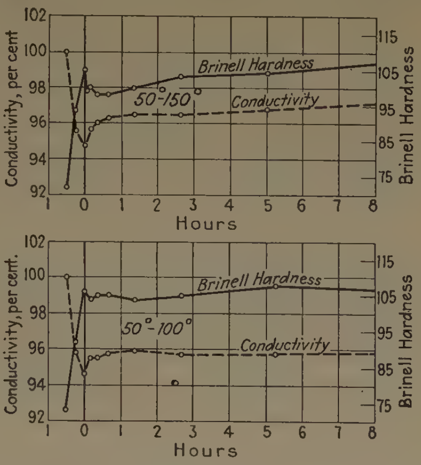

FIG. 11.

FIG. 10.—HARDNESS ANOMALY AFTER SUDDEN ELEVATION OF TEMPERATURE.
FIG. 11.—AGE-HARDENING ANOMALIES.

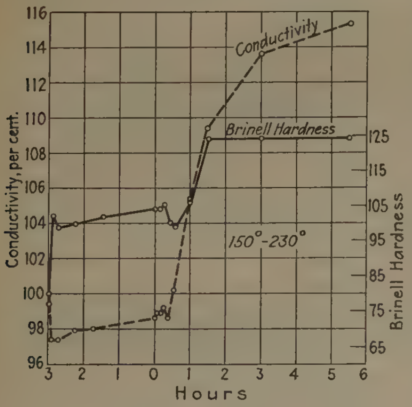

FIG. 12.—AGE-HARDENING ANOMALIES.

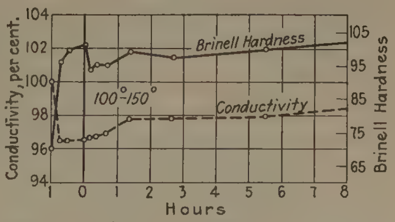

FIG. 13.—AGE-HARDENING ANOMALIES.

If the conditions are such that during the first treating at the lower temperature the conductivity finally becomes constant, it is at first maintained almost constant at the higher temperature (Fig. 13), while the hardness drops.

How can these phenomena be explained? G. Tammann has counted the nuclei in undercooled organic melts in the following manner. He first undercooled the melt to a low temperature at which nuclei are formed but crystal growth has not yet occurred. Then he heated it quickly to a higher temperature at which crystal growth takes place but nuclei are no longer formed. By this method he rendered the nuclei visible and by taking various low temperatures he could show the well-known curves of nuclei formation in dependence on temperature.

But M. Volmer and N. Weber[18] have pointed out that the minimum "critical size" of the nuclei at which they begin to be stable depends on temperature and consequently decreases with increased undercooling. Indeed, the stability jump from the supercooled liquid to the crystal increases with failing temperature and the free energy of the surface can be overcome at lower temperatures with smaller sizes of nuclei than at higher temperatures. It may therefore be expected that part of the nuclei formed at a lower temperature will become unstable when brought to the higher one. At this temperature only the larger nuclei will show further growth whereas the smaller ones will be *remelted* again.

The ideas of M. Volmer and N. Weber also relate to supersaturated solutions; for instance, to the aging of duralumin, since we can speak here also of nuclei, as we have shown above.

At the lower temperature, the size of the nuclei is small; it lies in the neighborhood of the "critical value." The formation of these nuclei reduces the thermal movement of the atoms of copper as discussed above and it is therefore not probable that there will be an appreciable *growth* of the nuclei at the lower temperature. When raised to a higher temperature, these nuclei will become unstable and again be dissolved. The formation of larger nuclei starts at once. But the diffusion involved in this process is more extensive than that required for dissolving small nuclei and therefore it proceeds more slowly. The number of distorted points in the space lattice will therefore be diminished and the hardness will decrease.

But as to this explanation, the objection may be raised that a simple coagulation (change of shape) of the nuclei can have the same effect. It seems unnecessary to make such complicated assumptions for explaining these observations. Again, this objection is contradictory to the behavior of the conductivity. If the conductivity decreases owing to the aging at lower temperature, this means that it is lowered by the nuclei formation. Its rise after being heated to the higher temperature can be explained just as well by the solution of some nuclei as by their "coagulation." But if the conductivity *rises* even at the lower temperature, as in

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[18] *Ztsch. phys. Chem.* (1926) **119,** 272.

Fig. 12, it is increased by the nuclei formation. The re-solution of the nuclei will therefore reduce the conductivity, but their coagulation will only accelerate its rise. The conductivity fall at the higher temperatures can only be explained by the re-solution of the nuclei in the way assumed for liquids by M. Volmer and N. Weber. If the conditions at the lower temperature are such that the conductivity is not at all changed by the nuclei formation, there is no reason why it should be changed at the higher temperature. It remains constant as in Fig. 13.

The experiments carried out by O. Dahl[19] with silicon-nickel alloys yielded similar results. The hardness anomaly after a rapid heating to a higher temperature can thus be easily explained by the theory of nuclei formation.

It is interesting that P. Merica, without knowing the results discussed above, assumed in his lecture of 1932 in connection with this phenomenon that the molecular process started during the aging at lower temperatures must in some way be reversed at the higher temperature.

We may on the same basis account for another anomaly also discovered by W. Fraenkel.[20] Assume that an age-hardenable alloy does not show a definite change of electrical conductivity when aged at room temperature immediately after quenching. Its conductivity *drops* by aging at the latter temperature if it has been aged partly at a higher temperature, say at 100° C. for aluminum alloys, and afterwards is aged at the lower temperature.

Now, although we do not know the exact cause of the decrease in electrical conductivity by aging at low temperatures, one thing seems to be sure; viz., that this drop in conductivity can be produced only by "knots" of extreme smallness and that larger nuclei, whatever their nature may be, will tend to *increase* the conductivity in accordance with the laws of heterogeneous equilibrium. If the aging decreases the conductivity, the "knots" formed will be, on the average, very small; if it increases the conductivity, as in duralumin at higher temperature, the nuclei on the average will be larger. If there is neither a decrease nor an increase in conductivity during aging, the smaller and the larger nuclei will be mixed in such proportions that on the average they will have no bearing on the result.

We assume that the distribution of the second metal in the mixed crystal is statistically irregular. But if we begin the aging at 100°, the formation of nuclei will proceed preferably at centers where large ones can be formed. When the aging begins later at the lower temperature, these large nuclei will remain as formed at 100° and the formation of small ones will be favored. This formation of small nuclei is accompanied by a drop in resistivity.

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[19] *Ztsch. f. Metallkunde* (1932) **24**, 277.

[20] *Ztsch. f. Metallkunde* (1929) **21**, 2–5.

The previous aging at a higher temperature must act as a lowering of the degree of supersaturation of the mixed crystal. If the interpretation given above proves correct, the same change as that produced by the previous aging at higher temperature can be obtained for an alloy having a smaller concentration of the second metal. This has been confirmed for the alloys of copper with beryllium. Fig. 14 shows that for the alloy with 3 per cent beryllium the electrical conductivity of the thin wire investigated first increases by aging at 250° C., while in the alloy with 2.5 per cent beryllium it decreases in the first ½ hr. of aging and in the alloy with 2 per cent beryllium in the first 4 hr. In connection with the matter discussed above, this shows that in alloys having lower contents of beryllium *small nuclei* predominate more than in those with higher contents of beryllium.

Thus far we have considered the formation of nuclei. We shall now discuss changes in the matrix crystal during or after the separation of nuclei. In this, we shall confine ourselves to comparatively large nuclei formed at higher temperatures where a second crystal phase is definitely produced. During its segregation the concentration and therefore, generally speaking, the lattice constant of the supersaturated mixed crystal, is altered.

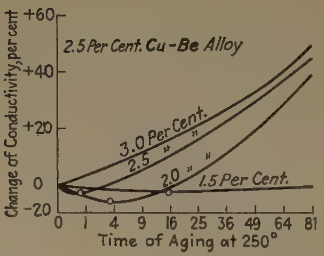

FIG. 14.

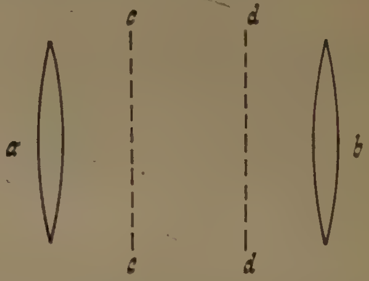

FIG. 15.

FIG. 14.—INFLUENCE OF BERYLLIUM CONTENT ON THE CHANGES IN CONDUCTIVITY WITH AGING.

FIG. 15.—SCHEME OF NUCLEI AND OF DIFFUSION.

Suppose that in a supersaturated mixed crystal there are two nuclei *a* and *b*, Fig. 15, of the second phase, say of $CuAl_2$ in a solid solution of copper in aluminum. Then the supersaturation will be eliminated in the neighborhood of *a* and *b*, whereas at greater distance, say between *cc* and *dd*, the supersaturated solution will be wholly unchanged at first. Diffusion will start between the parts richer and poorer in copper (of maximum and minimum copper content) and a continuous decrease of copper content will be developed gradually.

A continuous change of lattice constant corresponds to this decrease and on the X-ray film a broadening of the diffraction lines may be expected between the limits that correspond to the concentration at the beginning and at the end of the segregation process. This has been found true for the alloys of beryllium[21] and duralumin,[22] but in silver supersaturated with copper, Ageew, Hansen and Sachs[23] have found, as is well known, that during the process of the separation of copper crystals, instead of a gradual variation of the intermediate values of the lattice constant, there are two constants, corresponding to the beginning and to the end, respectively, of the segregation process. The intermediate values are present only to a much smaller extent, so as not to be clearly marked on the X-ray patterns.

One feels inclined to assume that this indicates another segregation process involving three phases, which is fundamentally different from the ordinary process observed in duralumin. But this is not so, as the following discussion will show.

Imagine that in the supersaturated silver there are regions where the separation can proceed more easily than in others. Such regions may lie at the corners of the crystals and the separation may occur in such manner that from certain single starting points (nuclei), crystal skeletons are formed as shown in Fig. 16. The branches of these skeletons lie very close together, whereas the distances between the single skeletons, as arising from different starting points, are much larger. In such a case the concentration between the branches of the skeleton will reach the saturation limit very rapidly, while in the areas between different skeletons it may be virtually unaltered. The segregation in these intermediate spaces will proceed much more slowly, either without further nuclei formation or with the formation of a few nuclei in the shape of plates, so that the diffusion paths used by the copper atoms to reach the nuclei are, on an average, much longer than the paths between the skeleton branches. But if the conditions are such that the nuclei remain plane plates, and the segregation proceeds in accordance with Fig. 12, the unaltered value will not be observed simultaneously with one in the saturated equilibrium condition. As a whole, of course, the process will be, retarded in this case.

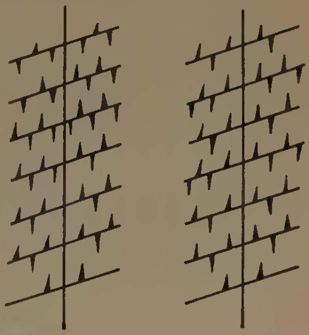

FIG. 16.—NUCLEI SKELETONS AND DIFFUSION SCHEME.

In copper saturated with silver, the last condition seems to be fulfilled with very large (single) crystals, and the first with fine crystals (polycrystalline material). With the single crystals the separation proceeds much more slowly than in the other case.[24] It seems therefore that with these conditions grain boundaries act as starting points for the formation of skeletons.

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[21] O. Dahl, E. Holm and G. Masing: *Ztsch. f. Metallkunde* (1928) **20,** 431.

[22] v. Göhler and G. Sachs: *Metallwirtschaft* (1929) **8,** 671–680.

[23] N. Ageew, M. Hansen and G. Sachs: *Ztsch. f. Phys.* (1930) **66,** 350.

[24] P. Wiest: *Ztsch. f. Phys.* (1932) **74,** 225.

The scheme given above also explains the other very striking observation made by Ageew, Hansen and Sachs, to the effect that a mixed crystal with segregated copper that has been cooled slowly from high temperatures again shows two distinct values of the lattice constant when reheated for a short time to a high temperature. In the neighborhood of the "nuclei" the branches of the skeletons evidently lie much closer to one another than in the intermediate regions, and the re-solution of the segregated copper is in the first case greatly accelerated in comparison with the second case.

These considerations on age-hardening may well be terminated with the following general remark. The process of aging and associated phenomena clearly shows, on the one hand, that a theoretical discussion of the problems involved offers great difficulties, since for the most part only qualitative statements are available and, on the other hand, that under these circumstances many contradictory results can be derived from the same theoretical basis, so that one must be very cautious in the introduction of new fundamental hypotheses in this field.

TRANSFORMATIONS

As to the problem of transformations of crystallized bodies, authorities today are chiefly interested in the question of the atomic mechanism; that is, the question of the path and intermediate atomic structure through which the body is transformed from the initial state into the final state. From this point of view, the problem has been studied by Mehl, Sachs, Weerts, Wever, Glocker, Dehlinger and many others. The results of these investigations show certain peculiarities of transformations in the metallic state—it seems that these are sometimes also found in nonmetallic bodies, which has raised some doubt as to their treatment from the standpoint of the laws of heterogeneous equilibrium and the phase rule and in this connection as to questions of terminology. Need is felt for some enlargement in this respect, but if this were done without sound precautions new difficulties might arise. The problem seems worthy of detailed discussion at this juncture.

I shall begin by reminding you of the definition of a thermodynamic phase as given by the great American physicist, Gibbs. With respect to a heterogeneous system, such as a salt solution, ice and vapor, or a melt and its crystals, he says:

> We may call such bodies as differ in composition or state, different phases of the matter considered, regarding all bodies which differ only in quantity and form as different examples of the same phase. Phases which can exist together, the dividing surfaces being plane, in an equilibrium which does not depend upon passive resistance to change, we shall call coexistent.

We see that this definition is a purely formal one; no mention is made of the nature of the properties which have different values for different phases. When a single property is, to a certain extent, different in different homogeneous bodies, while being constant in each of these bodies, it is sufficient to regard such bodies as different phases. The phases are *discernable* bodies of a heterogeneous system, while it is quite irrelevant whether we discern them on account of their color or space lattice or resistivity or some other physical property.

Now when Gibbs gave this definition of a phase he surely did not think of difficulties that might arise later. He thought of phases such as water and ice, or as the rhombohedral and the monoclinic modifications of sulfur, which show such strong differences in almost *all* properties that no doubt could arise as to their phase nature.

Later, the question of the atomic nature of phase differences and of the phase change arose and after the papers by Tammann and others had been published, it became customary to assume that different phases must differ in all their properties—if they did not do so in regard to a single property this was regarded as mere chance. For crystallized bodies the basis of this difference was a space lattice of different type for each particular phase. As to the formation of new phases from those already existing, the formation of nuclei and their growth was recognized to be the outstanding feature. With crystals, there was a formation of crystalline nuclei—starting points of the new phase—and their linear crystallization. As the types of space lattice in the two phases in equilibrium were considered to be quite different, a *complete atomic rearrangement* was thought necessary for germination. As to the linear crystallization, it followed the well-known laws of G. Tammann. It had the character of a *reaction velocity* and the factor determining it was the comparatively slow process of rearrangement of molecules from the unstable into the stable phase at the boundary between the two.

In this way and under the assumption that the germination number and the velocity of linear crystallization were constants in a given body, it was possible to calculate the whole process of transformation.

However, difficulties soon arose. One of the most interesting problems recently brought forward is that of the α-β magnetic transformation in iron.

The question as to the existence of two distinct phases, α and β, in iron has not been settled in spite of a long history of investigation. A. Westgren[25] and F. Wever[26] have shown that the space lattices of both α and β iron are the same. Since that time it has been assumed that there is no phase transition point between α and β iron in the constitutional diagram and that the change of properties (loss of ferromagnetism) proceeds smoothly over a certain temperature range.

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[25] *Ztsch. f. phys. Chem.* (1921) **98**, 181.

[26] *Mitt.* a. d. K. W. J. f. Eisenforschung (1922) **4**, 67.

But in 1925, Ruer[27] affirmed that on the cooling curve of very pure iron there is a real *arrest* point at the β-α transformation temperature. He concluded from his experiments that α and β are distinct phases and that therefore the theory of the phenomena given by P. Weiss[28] is erroneous so far as the neighborhood of the Curie point is concerned.

There seems to be a misunderstanding as to the last conclusion. The theory of Weiss makes an attempt to explain the heat development during cooling in the neighborhood of the Curie point purely by ferromagnetic changes. But the theory of Weiss makes no statement as to the question whether these changes occur at constant temperature or over a definite temperature range. Evidently Ruer held the opinion that a greater change must occur at this transformation point than the change involving magnetic phenomena alone.

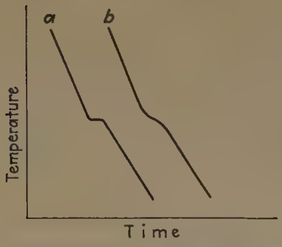

FIG. 17.—HOMOGENEOUS AND HETEROGENEOUS TRANSFORMATION.

F. Wever was not able to confirm the results of Ruer. With very pure iron, he detected heat evolution over a *temperature range* instead of at *constant temperature*. It seems, that the conclusions of Ruer have not been correct.

But let us assume for the sake of reasoning that Ruer's statement is correct; viz., that the cooling curve actually possesses the shape of *a* in Fig. 17 instead of the shape of *b*, as usually assumed. Does this mean that α and β are really different phases?

There is a slight, yet definite, heat of transformation. Iron in the α state is ferromagnetic, and in the β state, paramagnetic. But as to the other properties, these do not differ at all or at least only a little. The specific volume is slightly altered and in accordance with this, the dimensions of the space lattice; the other properties, as for example, the resistivity, show anomalies in the neighborhood of the α-β transformation point but, as it seems, no discontinuous change. The whole transformation undoubtedly can be understood to be the result of a spontaneous magnetization involving some slight changes of almost all properties.

If the cooling curve *a* is correct, this means that during transformation particles in the α state and others in the β state, the former showing spontaneous magnetization, will be in equilibrium with each other. Gibbs' formal definition of different phases evidently holds in this case. But what can be said about the nuclei formation and crystallization velocity?

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[27] R. Ruer and K. Bode: *Stahl und Eisen* (1925) **45**, 1184.

[28] P. Weiss and P. N. Beck: *Jnl. de. Phys.* [4] (1908) **7**, 279.

As for the first, one may perhaps speak of nuclei in a formal sense, as will be discussed later. But there is surely no rearrangement of atoms during the germination process. The structure remains unaltered —namely, a body-centered one—and the whole change consists in a very slight contraction. The state of affairs is much worse in connection with linear crystallization. There will be only a propagation of the ferromagnetic state, and to identify this with a velocity of linear crystallization would apparently be quite senseless.

We must therefore decide whether to maintain the formal definition of a phase as given by Gibbs, even if it will not yield any positive physical result, or to apply it only in the classical cases in which we can speak of germination and linear crystallization. For transformations such as α-β in iron a new classification and thus a new terminology must be provided.

It seems that the differences between transformations in the classical sense and those like the α-β transformation in iron—and we shall see later that in many other transformations similar features will be found—are today so strongly felt that it seems impossible and impractical to regard such cases simply as heterogeneous transformations. A line of demarcation must be traced; the pertinent question is: where, and how?

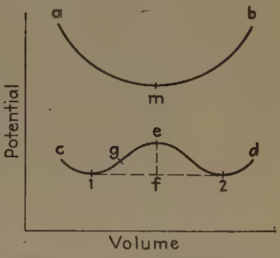

Fig. 18.—Homogeneous and heterogeneous equilibrium.

Let us now consider the possibility of using Gibbs' definitions in their formal significance.

If two different bodies—two phases—differing, say, in specific volume, are in equilibrium with each other, and continuous states with intermediate specific volumes do not exist, this means evidently that the latter are not stable, or at least are *less* stable, than the former.

We may discuss this case with the help of the thermodynamic potential of Gibbs in a manner analogous to that adopted by v. Rijn d. Alkemade[29] for binary systems (Fig. 18).

Let us first consider the curve *ab*. If we assume the state of the body to be changed at constant temperature and constant pressure, only that state corresponding to the minimum point *m* will be stable. The other states of the curve *amb* cannot be realized and differ materially from the states really existing in the neighborhood of *m* if both temperature and pressure are also changed. The change under consideration is also a "virtual variation" of the system that is often applied in thermodynamics.

Now the curve *ab* shows that *only one* state *m* can exist. The body under test will be homogeneous in the equilibrium state. The curve *amb* will apply, say, for a metal above its transformation temperature.

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[29] A. C. van Rijn van Alkemade: *Ztsch. f. phys. Chem.* (1895) **11,** 289.

But consider the curve *c1e2d* possessing equal minimum values of potential. Both corresponding states are therefore stable and can exist in equilibrium with one another, while the states with intermediate values are unstable. Indeed, a homogeneous body *e* has a higher potential value than it would have in a system consisting of two phases 1 and 2 (represented by *f*). In this case, the pressure would be the same at the points 1 and 2.

From this purely formal discussion, a conclusion may be drawn as to the way in which the second phase 2 can be formed from the first phase 1. Suppose that the system has the volume 1. We now increase the volume and the second phase 2 should be formed. But its formation can occur only with a certain retardation, because the nucleus of this second phase must first pass through the intermediate volume states of the curve 1*e*2 which, if at all possible, can only be achieved after overcoming strong atomic resistances. These resistances can be so strong as to give rise to a complete rearrangement of atoms after reaching a point *g*, or to the spontaneous formation of a nucleus of the phase 2. In other cases, all the intermediate states of curve 1*e*2 may be found in small component parts of the body, which have in some way (for example, by a maximum value of the kinetic energy of the molecules) been set up in this form.

While the formation of the first nuclei of the second phase is retarded, as this process is an improbable one, their further growth will occur without retardation. It is indeed highly probable that a body 2, if in contact with a body 1, may enable the latter to be immediately transformed into 2 without passing through the intermediate states of curve 1*e*2. When once formed the nuclei will grow with a fairly high velocity.

Hence we obtain the fundamental features of a heterogeneous transformation without further atomic assumptions. The first formation of a new phase is difficult and occurs only exceptionally; therefore, only at a few starting points. The further growth proceeds from these centers, acting as nuclei, without meeting with the obstacles encountered in their formation.

Without taking into account the mechanism of linear growth of the second phase 2, the upper value of its velocity is given by the heat development in the transformation process. This heat must in every case escape so rapidly as to maintain the temperature of the body below the point of transformation.

The features of germination discussed above result in the undercooling of a body and in the removal of this undercooling by germination.

Now let us proceed to a consideration of the fundamental features of metallic transformations. Up to the present, these have been discussed mainly on the basis of experimental data concerning, on the one hand, the iron-carbon alloys and, on the other hand, the gold-copper alloys, although they have also been found in many other alloys.

The most outstanding feature is that the new crystal body formed by transformation is often not oriented at random, but that its orientation is determined in a simple way by that of the body existing before the transformation under consideration. In the cases investigated up to the present, it is generally possible to indicate a very simple *homogeneous* mechanical deformation of the space lattice allowing the crystal to pass from the initial state to the final one. For example, the gold-copper alloy containing 50 per cent of each component, if cooled to about 430° C., undergoes a transformation from a cubic face-centered into a tetragonal face-centered space lattice. Every cubic crystal gives three tetragonal crystals whose shortened c axes are parallel to the [100] axes of the cubic crystal. The transformation can therefore be assumed to be the compression of a cubic crystal in the direction of one of its [100] axes, which is accompanied by a slight dilatation in the directions perpendicular to the shortened axis. Which axis of the three will actually be shortened at a given position in the crystal is a matter of chance, or, strictly speaking, of the external circumstances.

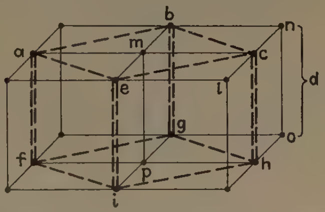

Fig. 19.—Face-centered and body-centered lattice.

Now in this case there is no breakdown and rearrangement of the space lattice and, accordingly, no germination in the molecular sense of the word. U. Dehlinger[30] and G. Sachs[31] draw therefrom the conclusion that the transformation cannot be described in terms of germination and linear growth.

In the γ-α martensitic transformation of iron-carbon alloys, Kurdjumow and G. Sachs have found[32] that the transformation of the face-centered cubic space lattice into the tetragonal space lattice of α martensite can be regarded as a shear deformation. It has not as yet been possible to find similar relationships of orientation in the transformation of pure iron, but it is highly probable that this is due to the recrystallization caused by stresses and strains during transformation, and it may be assumed that in general pure iron will behave in much the same way as the iron-carbon alloy.

As is well known, the body-centered cubic lattice can be represented as a face-centered tetragonal one.

Fig. 19 shows four elementary bodies of a body-centered cubic lattice (full lines), the lattice constant being d. The elementary body shown by dotted lines is that of a tetragonal space lattice whose tetragonal c axis is equal to d and whose a axes are $ab = bc = d\sqrt{2}$. The atoms lying in the middle of the diagonal planes (for example 1 in the plane *bchg*) are in the center of the elementary cube *mbncpgoh*, but in a side plane of the tetragonal body.

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[30] U. Dehlinger: Reference of footnote 16.

[31] *Ztsch. f. Metallkunde* (1932) **24,** 241.

[32] S. Kurdjumow and G. Sachs: *Ztsch. f. Phys.* (1930) **64,** 325.

With other ratios of $\frac{c}{a}$ than $\frac{1}{\sqrt{2}}$, the tetragonal *face*-centered space lattice does not correspond to the *cubic* body-centered, but to a *tetragonal* body-centered one.

Without entering now into a closer discussion of the shearing process of the γ-α transformation in iron, we may say that it can be regarded as a mechanism of transition from a face-centered *cubic* into a face-centered *tetragonal* crystal lattice.

We can represent both the formation of the cubic α iron and of the tetragonal martensite as a transition of this kind from the γ space lattice. It is a very interesting feature that the atoms of martensite may be assumed to lie between the initial position of the atoms in γ iron and their *final* position in the cubic α iron.

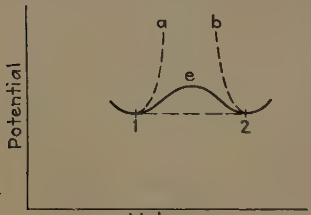

FIG. 20.

In cases such as the freezing of water or the transformation of one sulfur modification into another we cannot clearly visualize the intermediate atomic states after the beginning and before the end of a nucleus formation. Therefore the preceding potential curve has no real meaning with relation to the unstable conditions. It is accordingly more correct to refer these cases to a representation of potential, as given in Fig. 20, where the branches 1a and 2b rise rather abruptly. We are not able to make any definite assertion as to the state and the free energy conditions between a and b.

But if the transition from 1 to 2 can be described in such a simple way as a slight compression of a cubic lattice in the direction [100] and a slight dilatation in the two perpendicular directions, as in the compound Cu-Au, it is very probable that the path of the *homogeneous* transformation characterizes the transformation in the simplest manner and therefore will correspond to the lowest values of instability in the intermediate states. The stability of a compressed cubic lattice is, indeed, far greater than that of a broken down lattice, the latter corresponding perhaps to a highly undercooled liquid.

Furthermore, since it is quite certain that the transition path having minimum thermodynamic instability will really be followed, we can, in the case of metallic transformations of the type discussed, *indicate* the intermediate states occurring during transformation. In this case, and only in this case we therefore obtain a configuration 1e2 (Fig. 20) which deviates only slightly at point e from the straight line 1,2.

It is highly interesting to note that the formation of tetragonal martensite permits of indirectly checking this conclusion. A transformation of γ iron containing carbon into α iron involves two processes: the transformation of the space lattice and the diffusion of carbon, since the carbon content of the α iron is much smaller than that of the γ iron. Only when the excess of carbon has been segregated can the transformation take place in the cubic body-centered lattice. But if this segregation is avoided by acceleration of the transformation, as in the formation of martensite, the transition will be stopped midway; the cubic space lattice of α iron with higher carbon content being unstable. We have mentioned above that the space lattice of martensite may be regarded as a step in the process of the homogeneous deformation from γ to α iron. One step of this process is therefore found experimentally and we have still another reason to consider the intermediate stages of nuclei formation to be the states of an intermediate homogeneous deformation.

As a point of curve $1e2$ becomes stable by a comparatively slight change of the stability conditions due to the introduction of carbon into the iron, it is experimentally proved that the curve $1e2$ lies, in fact, only slightly above the straight line 1,2.

Now what can be said concerning the linear growth of the nuclei of the new phase? Since the whole transformation can be regarded as a simple mechanical deformation, the rearrangement of the lattice at the boundary of the nuclei will be very simple and can, in the atomic sense, by no means be called a "reaction." It is to be expected that this transformation will spread out rapidly. As the nuclei formation also proceeds much more easily than in "classical" transformations, the whole process must be a very rapid one. Sometimes it is, in the way mentioned above, practically regulated only by the heat balance of the process.

Since the two states before and after transformation differ only slightly from one another, metallic transformations of this kind have a small heat of transformation, as Dehlinger has pointed out.[33]

As to the nature of the linear growth of the second phase, we can affirm that in connection with copper-gold, this is, at least for single crystals, more properly to be compared with an elastic wave than with a velocity of reaction. The transformation extends from a "nucleus" in much the same manner as gliding or Lüders line in the tensile test spreads out from the point where the shearing has started, or as the shearing of a crystal in Iceland spar (Isländischer Spat) spreads out from the point where the crystal is compressed by means of a knife. The most striking feature of this kind of propagation of the "waves of transformation" is the formation of martensite needles; its velocity is, indeed, so high that up to the present it has not been possible to measure it even by means of a film camera.[34] We know from E. Scheil's[35] work that it is the shear stress that causes martensite to be formed from austenite. In this case it is indeed hardly possible to speak of germination, or of "crystal growth" in the same sense, as this is by common consent avoided in connection with the shearing of Iceland spar or the gliding process in metals.

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[33] U. Dehlinger: Reference of footnote 16.

But it must be remembered that between these two last processes, even though they resemble transformations, and the one just discussed, the most important difference is that in the latter we have the formation of a new body in a true thermodynamic sense.

We may now inquire whether these metallic transformations are really heterogeneous even from the standpoint of a formal definition. This question can only be answered when we can observe an equilibrium between the two phases that are transformed one into the other. In martensite this is impossible. But it is very likely to occur in the γ-α transformation of pure iron, in which certain properties are altered at constant temperature. At this temperature α and γ must therefore be in equilibrium with one another. Since, on the other hand, we have seen above that the γ-α transformation is one offering typical difficulties, a true heterogeneous transformation from the thermodynamic point of view can occur even if:

1. The orientations of the two phases stand in a simple relationship to one another.
2. The transformation can be regarded as a homogeneous mechanical deformation.
3. There is no germination in the sense of a breakdown of one atomic arrangement before the formation of another one.
4. The crystal growth does not reveal the atomic character of a velocity of reaction.

The fact that such a transformation is heterogeneous results in formation of the new crystalline variety from individual starting points with ensuing rapid propagation. We can therefore in this case still speak of the formation of nuclei and of their growth.

If the transformations were homogeneous, there would be no arrest on the temperature curve with pure substances, but rather a period of a retarded fall of temperature (Fig. 17, *b*).

The discussion of the question whether a transformation is homogeneous or heterogeneous is justified only with respect to equilibrium conditions that are in general not encountered in our experiments but may be extrapolated from our experimental results; usually these extrapolations may be considered justifiable. But it is interesting to notice that in the metallic phenomena under consideration the nature of the process will be appreciably different when we are far removed from the equilibrium condition (Fig. 21).

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[34] H. J. Wiester: *Ztsch. f. Metallkunde* (1932) **24,** 276.

[35] E. Scheil: *Archiv. f. Eisenhüttenwesen* (1928) **2,** 1.

The equilibrium condition for the transformation 1–2 is given at *a* in this figure. Here the potential values are equal for 1 and 2. If the system is somewhat undercooled, the potential of the phase stable at lower temperatures will be lower, as represented by *b*. The point *e* is still a low maximum and the states in its neighborhood are less stable than, for example, 1. At least part of curve 1*e*2 will therefore not be obtainable, just as in the equilibrium condition. But if the undercooling is more pronounced it may happen, as in Fig. 21, *c*, that curve 1*e*2 will not show a maximum. If we pass along this curve from the left to the right, successive points will correspond to states of increased stability. From a general point of view, it must therefore be possible to determine each intermediate state on curve 1*e*2, if we are able by any means to arrest the progress of reaction; for example, by quenching or by combining the transformation of the space lattice with another slow process such as segregation.

It is possible that these conditions are attained in the formation of martensite. The γ-α transformation of iron containing carbon is combined with the slow process of the separation of cementite. In this case, states 1 and 2 therefore differ not only in space lattice but also in carbon content. The separation of carbon can be prevented by quenching and we are thus able to establish an intermediate state, as discussed above.

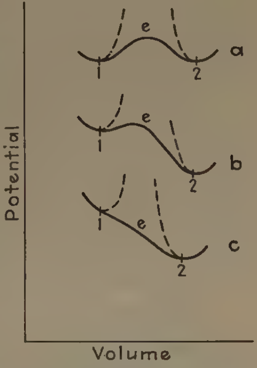

Fig. 21.—Change of transformation by undercooling.

It is possible that similar conditions are encountered in the compound gold-copper, where the slow process combined with the transformation of the space lattice is the formation of a regular atomic distribution.

There *may* therefore be cases of *heterogeneous* equilibrium of this kind in which the transformation is of a homogeneous character if it occurs at a point far enough removed from the equilibrium condition. The question is not yet settled whether such behavior will actually be realized in any of these transformations. If the intermediate states from the first possess a stability as low as we find in the "classical" transformations, it seems hardly possible that they should be obtainable by such a change of conditions.

If we now expect to draw conclusions as to the *classification* of transformations, it must be emphasized that, although there are pronounced differences between the transformations of the two kinds, as represented by sulfur and iron, many intermediate cases will doubtless occur. For example, although the different space lattices of the body experiencing a transformation often cannot be derived from one another after the simple manner of a homogeneous transformation, the orientations of the transformation products are nevertheless prescribed by the orientation of the mother body, as has been shown frequently by Mehl. Personally, I believe that this law will hold for almost all transformations. As to the mechanism, we must admit that this is likely to be more or less complicated. Mehl has shown that in the segregation of the compound $CuAl_2$ from duralumin, a simple mechanism can be found, but not one of homogeneous deformation. This field has not as yet been investigated and it is today impossible to say anything about the limitations of the two kinds of transformations.

It is my belief that transformations should be classified as follows:

The definition of the phase and of heterogeneous equilibrium as given by Gibbs must be employed in its purely formal sense. If two distinguishable homogeneous states of matter are in equilibrium with one another, their transitions are heterogeneous. The intermediate states are therefore unstable in the sense discussed above and the formation of the new phase begins at a few *starting points* and *spreads out* from these points. These two expressions are more general formulations of the terms, germination or formation of nuclei and velocity of linear crystallization. It is assumed that they are clear enough to express the view of Gibbs and are for the purposes of *general discussion* preferable to the other expressions, as they do not refer to the atomic conditions inherent in the latter.

The heterogeneous transformations, as defined above, are divided into two great groups which we may designate as nonmetallic transformations and metallic transformations. These expressions are designed to indicate the character of the process and the equilibrium involved therein rather than the group of chemical bodies in which they are found; in a similar sense, as, for example, the expression "metallic conductivity" characterizes the type of conductivity.

The nonmetallic transformations have a comparatively large heat of transformation, the alteration of properties is considerable and the intermediate states are highly unstable. It is not possible to describe them either atomically or thermodynamically. The difference of atomic arrangements in both phases is so great that it is not possible to indicate a simple mechanism of transformation. The starting points of the new phase are *nuclei* that are formed by the *rearrangement* of atoms. The spreading out of these nuclei has the character of a chemical reaction velocity and is called velocity of linear crystallization.

It may be assumed that the energy content of the intermediate state is in accordance with a complete breakdown of the crystal lattice; in other words, with the amorphous state. The energy of *activation* of the germination of the new phase will be of the same order of magnitude as the heat of crystallization of the melt. If the activation energy is known it will be possible to calculate the number of nuclei formed under given conditions.

The metallic transformations have, on the contrary, a small heat of transformation and a less pronounced change of properties. The intermediate state can be considered in terms of a quite simple atomic displacement. These metallic transformations may be assumed to be changes in which the displacement consists of homogeneous mechanical deformations. But it is almost certain that such a definition is too restricted. In the future it will be most important to find the true boundary between the atomic rearrangements corresponding to the two kinds of transformation.

The degree of instability of the intermediate states of material between two transformation steps is low, perhaps of the magnitude of mechanical strains. These states presumably can be obtained for short intervals of time, as compared with periods inherent in certain kinetic states in mechanics; as, for example, strains at the various points of an elastic wave. If the wave velocity of a material is about 1000 meters per second and the wave length 100 cm., the period of the wave will be 10^{-3} sec., and the duration of comparatively constant strains can be assumed to be of the order of magnitude of 10^{-4} sec., whereas in nonmetallic transformations the durations of unstable states can be compared with the lifetimes of unstable atomic configurations and must therefore be of the order of 10^{-20} seconds.

The weak point of the proposed classification lies in the fact that the nature of the boundary line between the two kinds of transformation is not yet definitely known and that there will probably not be a sharp limit at all, but rather a range of transition. Nevertheless, the suggested classification may be useful in the same way that the general classification of matter into metallic and nonmetallic bodies is in spite of the lack of a strict line of demarcation.

In the above discussion we have treated transformations alone and have dealt chiefly with pure metals and compounds. Analogous considerations will doubtless be applicable more generally to reactions in the crystalline state. These are generally associated with a change in composition of the transformed body which is in the nature of a slow process regulating the velocity of the whole reaction. These cases are more complicated than transformations without change of composition and are today being subjected to a most thorough investigation.

A Study of Segregate Structures in Copper-tin and Silver-zinc Alloys*

By D. W. Smith,† Pittsburgh, Pa.

(Buffalo Meeting, October, 1932)

The beta solid solution phases of the systems copper-zinc, copper-aluminum, copper-tin and silver-zinc are structurally analogous.[1] R. F. Mehl and O. T. Marzke[2] have shown that the α phase upon segregating from the β phase in the system copper-zinc takes the form of needles lying parallel to a [111] direction or some similar direction, such as [556], of the parent solid solution, and that the α phase upon segregating from the β phase in the system copper-aluminum also takes the form of needles. By analogy they assume that in this case also the segregate needles lie parallel to the [111] or [556] direction in the β lattice.

The purpose of this investigation is to determine whether the structures resulting from segregation of the α phases from the respective β phases of the systems copper-tin and silver-zinc are analogous to those obtained by Mehl and Marzke in the systems copper-zinc and copper-aluminum.

SEGREGATION OF THE α PHASE FROM THE β PHASE IN THE COPPER-TIN SYSTEM

Preparation of the Alloy.—An alloy containing 74.92 per cent (by weight) of copper and the balance tin was chosen for this investigation. This alloy, as can be seen from a portion of the constitutional diagram, Fig. 1, of the system copper-tin by Hamasumi and Nishigori,[3] with the proper heat treatment should segregate the α phase out of the β parent solid solution phase. The alloy was prepared from high purity cathode copper (analyzing 99.98 per cent Cu) and Straits tin (analyzing 99.94

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* A part of a dissertation presented by D. W. Smith to the Faculty of the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

† Assistant Metallurgist, Bureau of Metallurgical Research, Carnegie Institute of Technology.

[1] A. Westgren: Untersuchungen über den Aufbau Metallischer Systeme mittels Röntgenstrahlen. *Ztsch. f. Metallographie* (1930) **22**, 368.

A. Westgren: X-ray Determination of Alloy Equilibrium Diagrams. *Trans.* A.I.M.E. (1931) **93**, Inst. of Metals Div., 13.

[2] R. F. Mehl and O. T. Marzke: Studies upon the Widmanstätten Structures, II. *Trans.* A.I.M.E. (1931) **93**, Inst. of Metals Div., 123.

[3] M. Hamasumi and S. Nishigori: On the Equilibrium Diagram of Copper-Tin Alloys. Tohoku Imp. Univ. *Tech. Repts.* (1931) **10**, 131.

per cent Sn). The mixture was melted (tin added after the copper was melted) in a graphite crucible under a borax flux in a gas-fired pot furnace. The molten alloy was thoroughly stirred with a fused silica rod and allowed to cool slowly in the melting crucible, in order to obtain a coarse-grained structure. This procedure was followed because this alloy is very hard and brittle and the method of obtaining

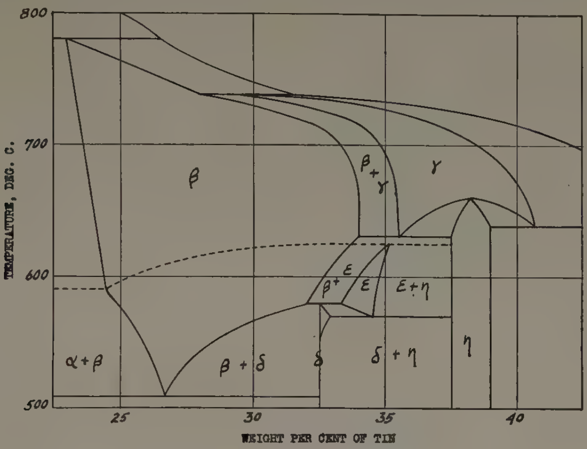

FIG. 1.—A PORTION OF THE CONSTITUTIONAL DIAGRAM OF THE SYSTEM COPPER-TIN. (*Hamasumi and Nishigori.*)

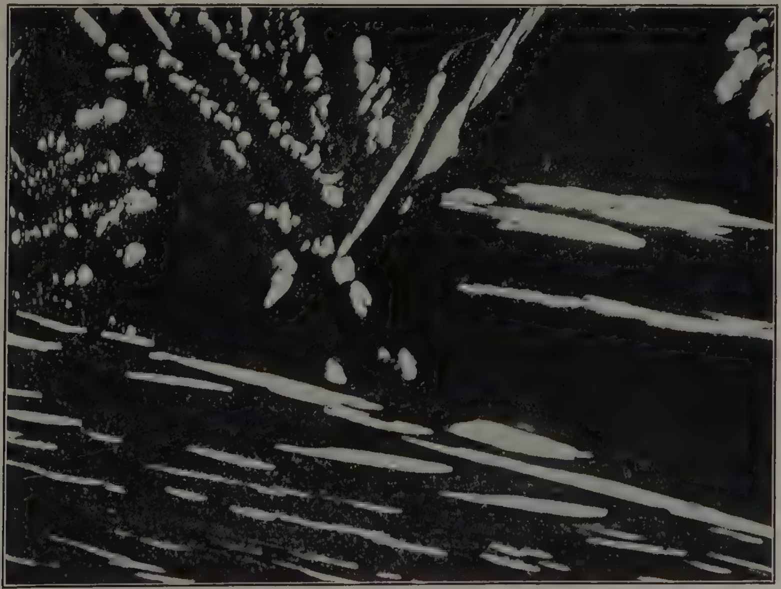

FIG. 2.—STRUCTURE PRODUCED BY THE SEGREGATION OF THE α PHASE FROM THE β PHASE OF THE COPPER-TIN ALLOY. × 50.

a coarse-grained structure by the process of straining and annealing is not applicable.

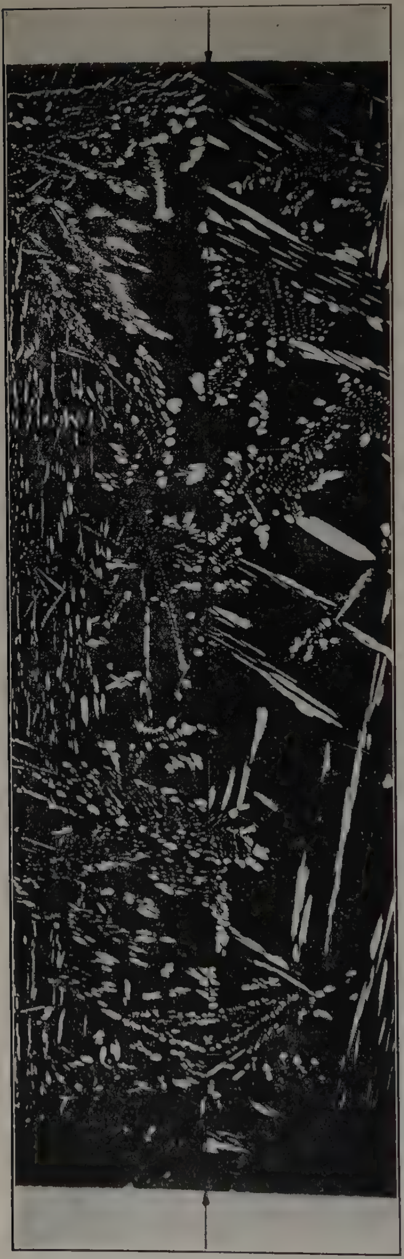

Fig. 3.—Composite photomicrograph of the copper-tin alloy showing two surfaces cut at 90° to each other. Arrows indicate the edge between the two surfaces. × 50.

Various heat treatments were tried in order to determine the proper conditions for formation of a well defined segregate structure. It was found that by annealing at 700° C. for 2 hr., then allowing furnace cooling to 550° C. and finally quenching in water, the desired structure was obtained (Fig. 2). The final quench from 550° C. was necessary because this alloy suffers a eutectoid inversion at 508° C. (Fig. 1).

Form of the Segregate.—Several specimens, each containing large grains exhibiting well defined segregate structures, were cut and polished on two surfaces at 90° to each other. The two surfaces were inspected under a microscope at and immediately adjacent to the edge between them, using oblique (45°) illumination. With this technique it was found that the segregate was needlelike and not of plate or polyhedral form.

Fig. 3 is a composite photomicrograph of one of these grains polished on two surfaces mutually at right angles. It shows the α segregate needles (light in the photomicrograph) on the two polished surfaces with the edge between the two surfaces (indicated by arrows) passing through the center. It can be seen that α segregate particles making long traces on one surface do not pass over the edge on to the other surface; indicating, of course that, the segregate is of needle form. However, on the left-hand side of the photomicrograph can be seen a set of needles which do not possess long traces on either surface of polish but appear to line up so as to indicate the presence of a plate or lamella.

Crystallographic Direction [hkl] of α Segregate Needles.—For the determination of the crystallographic direction in the β matrix along which the α phase segregates, a grain was chosen which exhibited several well defined traces of the segregate needles on the surface of polish. The orientation of the β matrix with respect to the surface of polish and a suitable reference scratch was determined by means of the Davey-Wilson X-ray method.[4]

Fig. 4 is a stereographic projection of the grain with the surface of polish coincident with the plane of the projection and the reference scratch parallel to the horizontal diameter marked "Reference Line." The poles of the isometric forms {110}, {111} and {112} are shown by small circles marked with the Miller indices of form. The traces which the segregate needles delineated on the surface of polish appear as dashed lines. The longest and best defined traces made by the needles on the surface of polish are AA' and BB'.

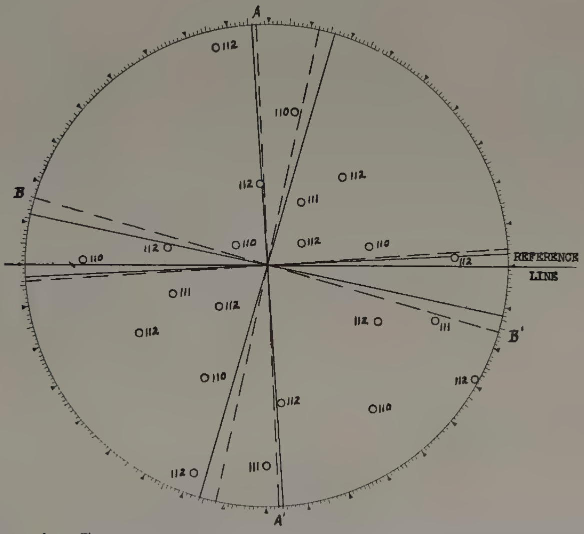

FIG. 4.—STEREOGRAPHIC PROJECTION OF β COPPER-TIN GRAIN.
Dashed-line diameters represent directions taken by α-segregate needles. Solid-line diameters represent normals to these directions.

From the projection it can be readily seen that these traces lie very close to poles of planes of the form {111} which are themselves near the periphery of the projection. The normals (full lines in Fig. 4) to all traces pass, with a high degree of accuracy, through poles of planes of the form {112}. These planes in the β matrix lie in a zone surrounding a

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[4] T. A. Wilson: A Study of Crystal Structure and Its Application, XII. *General Elec. Rev.* (1928) **31,** 612.

[111] direction, and the normal to any trace made by the segregate needle lying along a given crystallographic direction must necessarily pass through the pole of some plane lying in the zone surrounding that given direction; therefore it appears most likely that the α phase on segregating out of the β phase takes the form of needles parallel to [111] directions of the β phase.

Twin Bands in the β Phase.—During the course of the preparation of specimens for this investigation it was found that the β phase of the copper-tin alloys twinned readily as a result of a very small amount of strain, such as that produced by the scratching of a polished surface with a sharp pointed scribe (Fig. 5) or by cutting out a section with a hacksaw. This twinning was confined to areas adjacent to the application of stress and did not penetrate deeply into the specimen, probably because of the hard, brittle, nonplastic character of the β phase.

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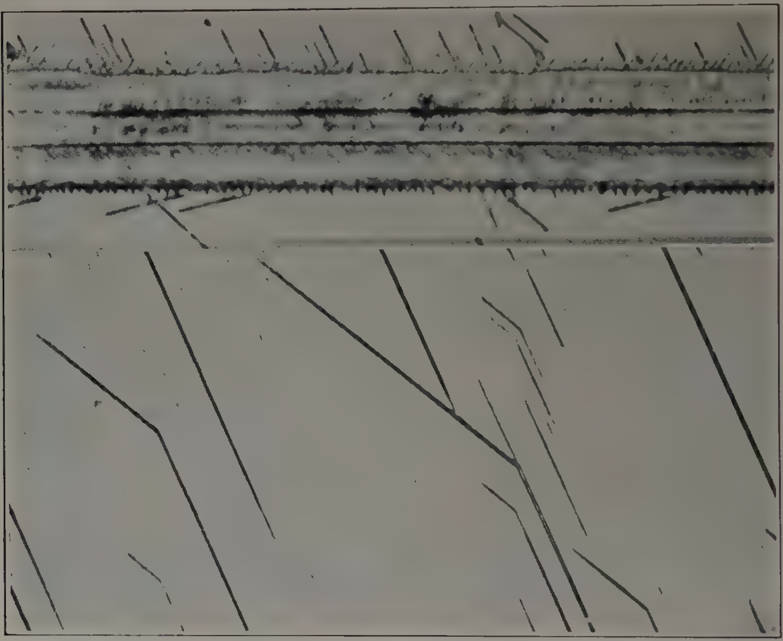

FIG. 5.—TWINS IN THE β PHASE OF COPPER-TIN ALLOY RESULTING FROM A SCRATCH MADE BY A SHARP POINTED SCRIBE. × 275.

FIG. 6.—SAME SPECIMEN AS IN FIG. 5 AFTER ANNEALING 2 HR. AT 700° C. WITH A SUBSEQUENT QUENCH IN WATER. × 275.

When a specimen, strained as described above, was heated to a temperature well up into the β field (700° C.) and held at that temperature for 2 hr. with a subsequent quench in water, the twins appeared to grow in size and penetrated farther into the specimen, as shown in Fig. 6. In order to study this structural feature a specimen was chosen which contained two large grains revealing many twin bands in the two surfaces of polish at right angles to each other. The orientations of the grains were determined in the usual manner with respect to one surface of polish and the edge by means of the Davey-Wilson X-ray method. Figs. 7*a* and 7*b* are stereographic projections of the two grains; in each case one surface of polish (hereafter referred to as the first surface) is in the plane of the projection and the other surface of polish (hereafter referred to as

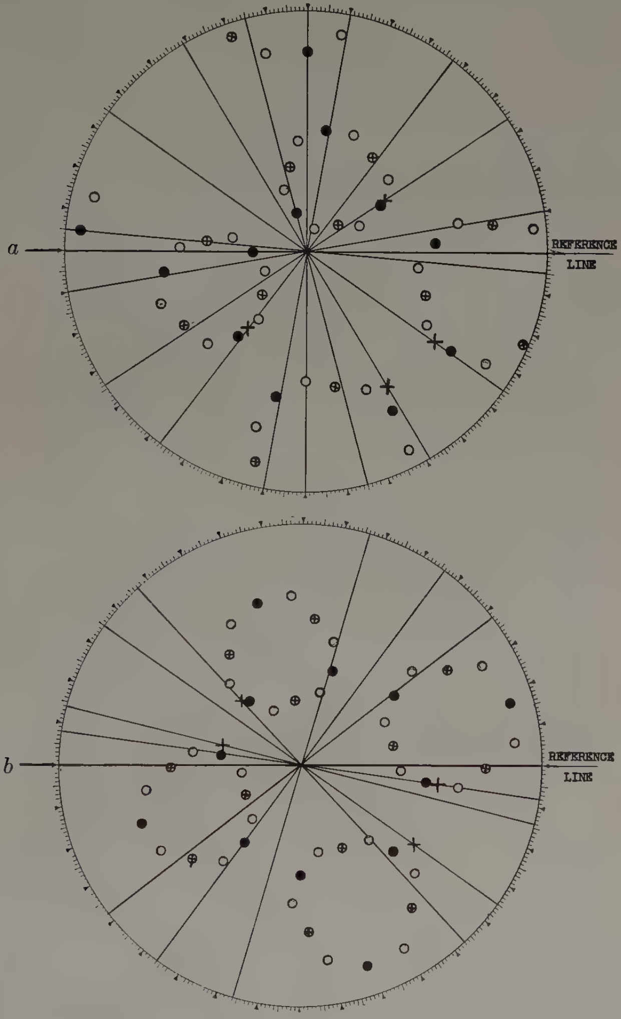

FIG. 7.—STEREOGRAPH PROJECTIONS OF β COPPER-TIN GRAINS.
Circles represent poles of planes of the form {123}.
Crossed circles represent poles of planes of the form {112}.
Filled circles represent poles of planes of the form {133}.
Solid-line diameters represent normals to directions of twin bands in first surface of polish.
Crosses represent poles of the twin planes.

the second surface) at right angles to the first, is represented by the horizontal diameter of the projection—the reference line.

Normals to the traces made by the twin bands on the first surface were plotted on those projections and appear as straight-line diameters. The poles of the twin planes, which could be traced accurately on the two surfaces of polish and over the edge, are represented by crosses in the projections. Although the coincidence of these crosses with poles of the {133} form is not particularly satisfactory, it is sufficiently accurate to indicate that the plane of twinning in the β phase of the copper-tin alloys is definitely not the {112} family of planes as is the body-centered cubic ferrite. The possibility of the {123} family constituting the twinning planes was considered, but the fact that the maximum number of traces observed within a single grain on a given surface of polish was 11 is against this assumption because this family of planes yields 24 traces. It would seem that more than one-half of these should actually be observed in a specimen cut at random. It therefore appears reasonable to assume that the plane of twinning in the β phase of copper-tin alloys is actually of the form {133}, requiring a maximum of 12 traces. Fig. 8 graphically represents this possibility of mechanical twinning on the {133} plane of the body-centered cubic lattice.

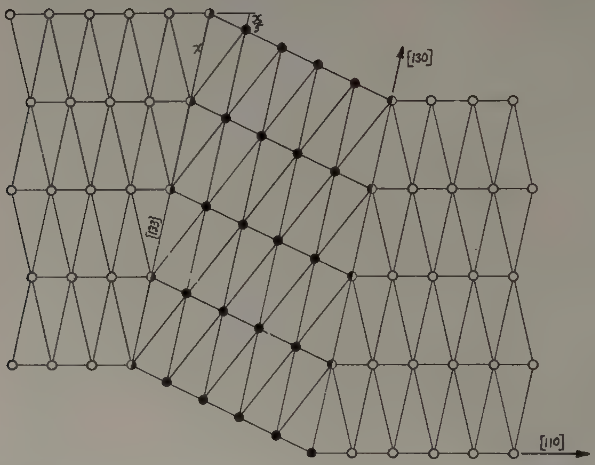

FIG. 8.—REPRESENTATION OF TWINNING ON {133} PLANES IN A BODY-CENTERED CUBIC LATTICE. PLANE OF PROJECTION {133}.

Pseudomorphic Segregation of the α Phase along Twin Bands of the β Phase.—The specimen which has just been described with reference to the location of the plane of twinning was heat-treated to segregate the α phase. It was found that annealing the specimen at 550° C. for 2 hr. with a subsequent quench in water brought out the desired α phase in the form of plates along the twin planes, and that the twins were no longer apparent but had apparently been obliterated during the process of segregation. Fig. 9 is a photomicrograph of this structure showing the α segregate appropriating positions formerly occupied by twins according to check measurements made as in the original determination of the twinning plane. Following these check measurements, the orientation of the grain was redetermined by the Davey-Wilson X-ray method

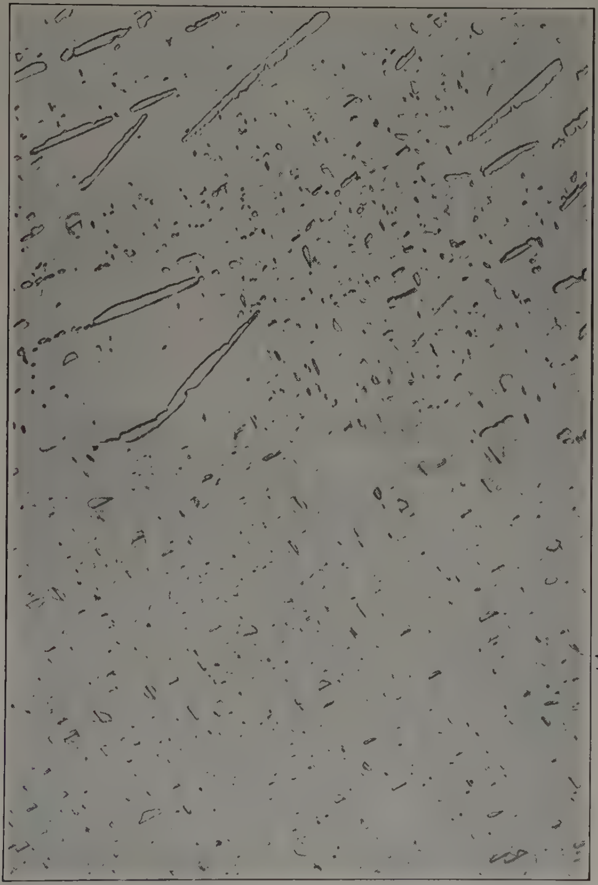

FIG. 9.—PSEUDOMORPHIC SEGREGATION OF α PHASE ALONG PLANES ORIGINALLY OCCUPIED BY TWINS. × 150.
FIG. 10.—OCCURRENCE OF TWINS IN THE α SEGREGATE. × 150.

and it was found that no change had occurred other than some slight distortion as evidenced by "fuzzy" reflections.

Orientation of the α-phase Segregate with Respect to the β-phase Parent Solid Solution.—With the proper heat treatment, the α phase could be segregated from the β phase in the form of small rounded particles, practically all of which contained twin bands (Fig. 10). This occurrence of twins in the α segregate opened up an avenue for determination of the orientation of the segregate with respect to the matrix material, which otherwise would have been impossible or at least extremely difficult, as generally recognized in problems of this sort.

It is a well-known fact that the α phase twins on {111} planes, and it is not difficult to determine, by means of X-ray and stereographic methods, which plane in the β-phase matrix is parallel to the twinning plane {111} so clearly revealed in these particles of α segregate.

A specimen was chosen and polished in two surfaces at right angles to each other and the angles made by the traces of the twins with the edge between the two surfaces were accurately measured. The full line diameters, in Fig. 11, represent normals to traces of the twins made on the surface of polish which is in the plane of projection and the great circles represent normals to traces of the twins made on the surface at right angles to the plane of projection and whose projection is the horizontal diameter, or reference line.[5]

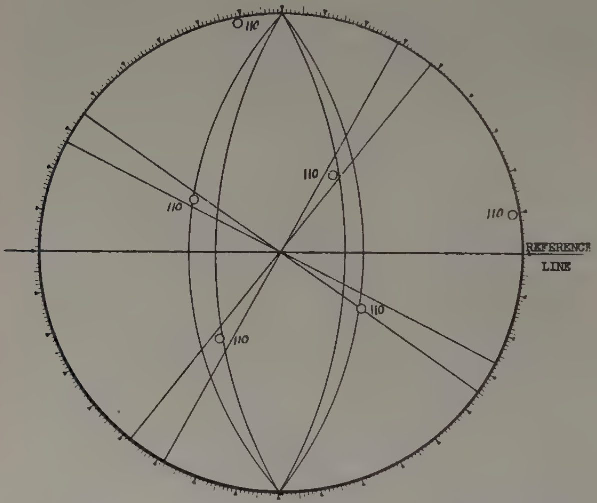

Fig. 11.—Stereographic projection of β copper-tin grain.

Solid-line diameters represent normals to directions of α twins on surface in plane of projection.

Great circles represent normals to directions of α twins on surface at 90° to plane of projection.

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[5] This method of stereographic analysis was used by N. T. Belaeiw [*Jnl.* Inst. of Metals (1923) **29,** 379] and R. F. Mehl and C. S. Barrett [*Trans.* A.I.M.E. (1931) **93,** Inst. of Metals Div., 78].

The locus of poles of all planes capable of producing a given trace on the surface of polish which is in the plane of the projection is represented by a straight-line diameter while the locus of poles of all planes capable of producing a given trace on the surface of polish at 90° to the plane of the projection and whose projection is the diameter labelled "Reference Line," is represented by a great circle whose diameter is

The orientation of the β-phase matrix was determined by the Davey-Wilson X-ray method and the poles of {110} planes of the matrix were plotted on the projection. The intersection of a normal to a trace on one surface with the normal to a corresponding trace on the surface at 90° to the first represents the pole of a plane which would give these traces on the two surfaces. As can be seen in Fig. 11, a proper choice of intersections yields poles of (twinning) planes almost exactly coincident with {110} poles of the β matrix.

The family of {110} planes is a simple set (with a maximum of six traces on a surface cut at random) and there is no reason to believe that we are dealing with more complicated planes of higher indices, which might conceivably be admitted within the limit of error of the above analysis. It therefore seems safe to assume that the α phase segregates out of the β phase with a {111} plane parallel to a {110} plane of the β phase.

SEGREGATION OF THE α PHASE FROM THE β PHASE IN THE SILVER-ZINC SYSTEM

Preparation of the Alloy.—An alloy containing 67.76 per cent silver (by weight) and the balance zinc was chosen for this investigation. This alloy, as can be seen from a portion of the constitutional diagram, Fig. 12, of the system silver-zinc by Guillet and Cournot,[6] with the proper heat treatment will segregate the α phase out of the β parent solid solution phase. The alloy was made up from high purity electrolytic silver and C.P. triple distilled zinc. The zinc was melted first in a graphite crucible under a protective cover of charcoal in a gas-fired pot furnace. When the zinc melted the silver was added slowly and stirred into the melt while at the same time the temperature was increased to keep the mixture molten. The molten alloy was thoroughly stirred with a fused silica rod and allowed to cool slowly in the melting crucible in order to obtain a coarse-grained structure and to

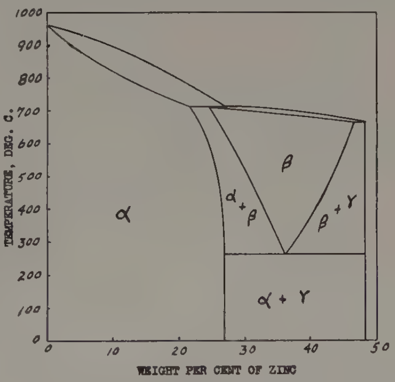

FIG. 12.—A PORTION OF THE CONSTITUTIONAL DIAGRAM OF THE SYSTEM SILVER-ZINC. (*Guillet and Cournot.*)

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determined by the complement of the angle which the trace made with the edge between the two surfaces. The pole of the plane sought is found at the intersection of the straight line diameter and the corresponding great circle.

[6] S. Guillet and J. Cournot: Influence of Heat Treatments on Certain Alloys of Ag-Zn and Ag-Cd. *Rev. de Mét.* (1930) **27**, 1.

assimilate, as nearly as possible, the same conditions as those under which the copper-tin alloy was prepared.

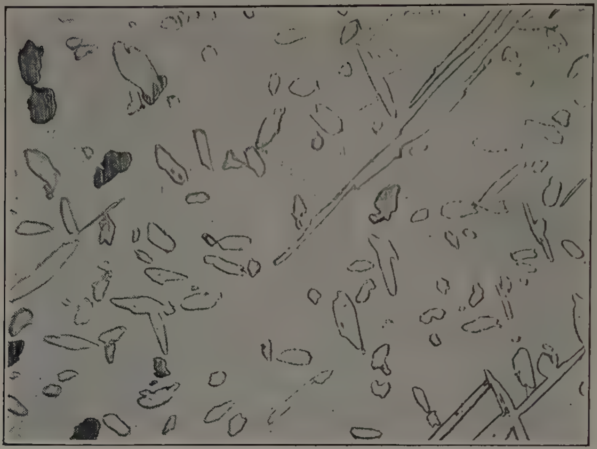

FIG. 13.—STRUCTURE PRODUCED BY THE SEGREGATION OF THE α PHASE FROM THE PHASE OF THE SILVER-ZINC ALLOY. × 50.

Various heat treatments were tried in order to determine the proper conditions for formation of a well defined segregate structure. It was found that by annealing the alloy at 630° C. for 24 hr. and then transferring it to another furnace at 315° C., retaining it at that temperature for 2 hr., and finally quenching it in water from that temperature, a well defined segregate structure was developed, as illustrated in Fig. 13.

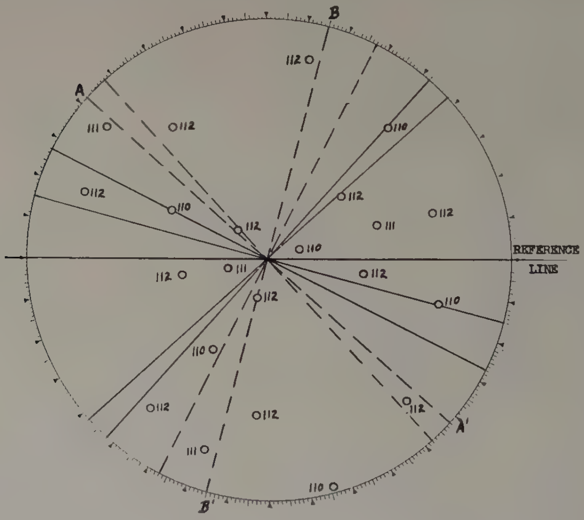

FIG. 14.—STEREOGRAPHIC PROJECTION OF β SILVER-ZINC GRAIN. Dashed-line diameters represent directions taken by α segregate needles. Solid-line diameters represent normals to these directions.

The quench in water from 315° C. was necessary as the β-phase matrix material suffers a eutectoid inversion at 264° C. (Fig. 12).

Form and Crystallographic Direction [*hkl*] *of* α *Segregate.*—The same method of procedure was applied to this alloy as to the copper-tin alloy. It was again found that the α phase segregated from the β-phase matrix in the form of needles. Fig. 14 is a stereographic projection of the grain chosen for investigation. The orientation of the grain was determined, as in previous cases, with respect to the surface of polish, which is in the plane of projection, and a reference scratch which is parallel to the horizontal diameter of the projection, or "reference line."

The traces made by the segregate needles on the surface of polish were plotted and appear as dashed-line diameters. The longer and better defined traces are AA' and BB'. These directions lie very close to poles of planes of the form $\{111\}$ which are situated close to the periphery of the projection. Normals to these traces, appearing as solid-line diameters in the projection, are accounted for by poles of planes which lie on a zone surrounding [111] directions and therefore, just as in the copper-tin alloy, it appears most likely that the α phase on segregating out of the β phase takes the form of needles parallel to [111] directions of the β phase.

Unsuccessful attempts were made to produce twin bands in the β phase of the silver-zinc alloy, as was done in the copper-tin alloy. Various heat treatments were also conducted in an unsuccessful effort to produce twins in the α-phase segregate. However, judging from the results of the investigations on these two systems, it appears reasonable to assume that the α-phase segregates in the two systems have the same crystallographic relationships to their respective β-phase parent solid solutions.

THEORETICAL CONSIDERATIONS OF THE RESULTS

In both alloy systems studied (copper-tin and silver-zinc) it was found experimentally, that the α phases, on segregating from their respective β phases, form as needles along [111] directions of the β-phase parent solid solution, and also in the copper-tin system that $\{111\}$ planes of the α-phase segregate lie parallel to $\{110\}$ planes of the β parent solid solution phase. By analogy, it is assumed that also in the silver-zinc system $\{111\}$ planes of the α-phase segregate lie parallel to $\{110\}$ planes of the β parent solid solution phase.

The fact that in both of these systems, copper-tin and silver-zinc, and in the systems investigated by Mehl and Marzke, copper-zinc and copper-aluminum, the α-phase segregates formed as needles along [111] directions, the direction of densest atomic packing in the body-centered-cubic system, of the β-phase matrices, indicates that an analogous condition of atomic matching between the two respective participating phases must be an essential object of consideration in theorizing on the mechanism of formation of segregate structures in these alloys. Not only in these alloy systems but also in all systems thus far reported on, with the single exception of the iron-nitrogen system, crystallographic directions of densest atomic packing are found in the planes of segregation.

Fig. 15 illustrates the atomic arrangement of the {110} plane of the β-phase matrix and of the {111} plane of the α-phase segregate of the copper-tin system superimposed on one another. The atomic matching of these planes in the silver-zinc system is nearly identical. It can be readily seen from this figure that there is a very close atomic matching between [111] directions of the β phase and [110] directions of the α-phase segregate in the copper-tin system, which is also true for the silver-zinc system; in fact, the interatomic distances in these two directions differ by only 1.5 per cent in the copper-tin alloy and by only 1.8 per cent in the silver-zinc alloy. On the other hand, while the atomic matching of a {110} plane of the β matrix with a {111} plane of the α segregate is very unsatisfactory, as can be readily seen, no other planes superior in this respect could be discovered.

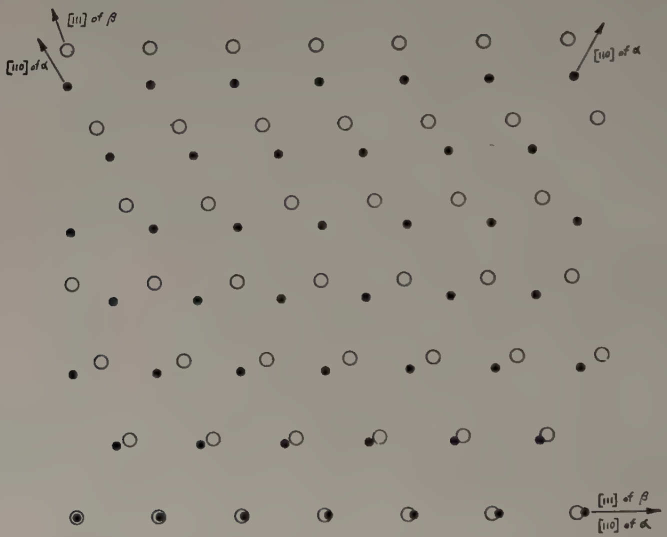

Fig. 15.—Atomic arrangements on {110} planes of the β-phase matrix and {111} planes of the α-phase segregate in the system copper-tin, superimposed on one another.

Circles represent atoms of the β phase; dots represent atoms of the α phase.

With these facts in mind it can be postulated that the α phase on segregating from the β phase orientates itself so that a {111} plane lies parallel to a {110} plane of the β phase and a [110] direction parallel to a [111] direction of the β phase. Since the atomic matching between the two parallel planes in the two phases is not good, the tendency of the original nucleus to grow into a well developed plate will be weak and plate formation in such alloys will seldom occur. However, the atomic matching of the two significant (close-packed) directions in these two phases may be termed satisfactory and therefore the original segregate nucleus will grow rapidly and easily in this [111] direction of the β phase, thereby forming a well developed needle.

It is also conceivable that these needles might, depending on the conditions of formation, readily line up or coalesce to form plates of segregate parallel to some plane in the matrix located in the zone whose axis is the primary growth direction [111]. Conditions exerting an influence on such a process of coalescence of needles to form plates might be concentration, temperature of formation of the segregate, and stresses set up by segregation. Mehl and Marzke[7] obtained, in a 57.3 per cent Cu brass, α segregates which showed only a slight tendency toward plate formation, while A. J. Phillips[8] showed that a higher copper concentration accounted for a decided tendency for the α segregate to form plates. Temperature of formation of the segregates undoubtedly has an effect on the resulting form of the segregate, as it is well known that various heat treatments, while yielding the same basic segregate structure, have a great effect on the size and detailed configuration of the segregating phase particles. In many of the published photomicrographs of segregate structures there appear fairly large local areas containing particles of apparently the same orientation with few if any segregated particles of another orientation visible. This phenomenon is probably due to local stresses created by the initial segregations which have controlled the orientation of the segregated particles.

From the results of this investigation and the investigations of Mehl and Marzke it is apparent that the segregate structure resulting from the separation of the α phases from the respective β phases in the systems copper-zinc, copper-aluminum, copper-tin and silver-zinc are analogous in their mode of formation and general development.

Acknowledgment

The investigations outlined in this paper were carried out at the Hammond Laboratory, Yale University, under the direction of Prof. C. H. Mathewson, to whom the author is greatly indebted.

DISCUSSION

(Sam Tour presiding)

R. F. Mehl, Pittsburgh, Pa. (written discussion).—Dr. Smith has made two important additions to this subject: he has shown that the Widmanstätten figures formed by the precipitation of the α phases from the β in the copper-tin and silver-zinc systems are both structurally analogous to those noted by Mr. Marzke and myself for the systems copper-zinc and copper-aluminum, and he has demonstrated the relationship in orientation between the α precipitate and the β matrix phase—the first demonstration of this relationship in systems of this type. The method used for the determination of the orientation of the α phase—by the use of twin bands—is very ingenious.

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[7] Reference of footnote 2.

[8] A. J. Phillips: *Trans.* A.I.M.E. (1931) **93,** Inst. of Met. Div., 152.

It is to be expected that the Widmanstätten figures in these systems should be analogous in form, for, as Westgren has shown, the phases participating in the formation of these figures are structurally analogous. Indeed, we may probably now safely conclude that when the phases participating in the formation of a segregate structure are structurally analogous, the segregate structures formed are also structurally analogous.

With Dr. Smith's demonstration that the (110) plane in the β phase is parallel and in atomic positions in coincidence with the (111) plane in the α phase, some reason for the pronounced acicular structure form of the α segregate should be easily found. The theory the author advances—that growth into true needles results from a poor match in atomic positions upon the two atom planes but an excellent match along the atomic directions in these planes—is interesting, but leads immediately to a number of questions difficult to answer:

Why is it that the direction of the α needle in the β matrix is not exactly [111] though near to it, and why are there at least two needles near each [111] direction, the lattices of which are not of the same orientation? These were among the most carefully made observations in Mr. Marzke's work and I think cannot be disregarded.

Furthermore, this reason for the formation of true needles could also be advanced for the precipitation of the α phase from the γ in the iron-nickel system (the Widmanstätten figure in meteorites), for in this case also the (111) atom plane in the face-centered cubic (γ) phase is parallel and in coincidence with the (110) plane in the body-centered cubic (α) phase with approximately the same difference in atom spacing—2 per cent—in the [110] direction and [111] direction in the two phases. Yet these alloys form well defined plates, not needles.

The chief difference in the two cases is in the direction of the precipitation; in iron-nickel alloys the body-centered phase precipitates from the face-centered whereas in the copper-zinc alloys, etc., the face-centered precipitates from the body-centered. We may then well ask whether with identical crystallographic relationships precession is important, whether reversal in order may not lead segregate structures of different external form. Such a reversal has already been noted in the copper-zinc system with the β and γ phases, and in this case the types of Widmanstätten figures are indeed different.[9] A photomicrograph published by W. P. Sykes illustrating the formation of the face-centered cubic γ phase from the body-centered cubic α-δ phase in the iron-tungsten system[10] shows the γ phase to take an acicular form surprisingly similar in appearance to those shown by Mr. Marzke and the present author. Although we have no photomicrograph of the reverse precipitation, we may probably safely assume that it leads to the formation of true plates as in the other systems of iron. We may well suspect, therefore, that the order of formation is of great importance in determining the outward form of the segregate; present theories of Widmanstätten figures do not explain this behavior and may therefore have to be modified.

The proof of mutual orientation given in Fig. 11 is not complete and therefore somewhat open to question. In this figure there is plotted the projections of the normals to the traces of four (111) (twinning) planes in the α phase; these come into coincidence with the projections of four (110) planes in the β phase, and this is taken as proof of such a mutual orientation. The fact of this coincidence of projections, however, is a demonstration that the (111) projections of the α phase were not derived all from one α grain or one orientation of α, for (111) projections cannot be brought into coincidence from (110) projections.

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[9] Reference of footnote 2, 141, Fig. 18.

[10] W. P. Sykes: Composition Limit of the Alpha-gamma Loop in the Iron-tungsten System. *Trans.* A.I.M.E. (1931) **95**, Fig. 7.

Furthermore, it cannot be certain that the intersections chosen of the normals to the traces of the (111) planes are properly selected. Although it seems quite likely that Dr. Smith's solution is the proper one, the crystallographic proof advanced cannot be considered complete. Without doubt Dr. Smith has done the best he could under the circumstances.

The Precipitation of Alpha from Beta Brass*

By Oscar T. Marzke, Lansing, Mich.

(New York Meeting, February, 1933)

Abstract

Four alloys that precipitate the alpha phase from the beta of the copper-zinc system were heat-treated in various ways to develop as many forms of the segregate as possible. It was found that the precipitate may have the form either of plates or of needles. Plates usually result when precipitation occurs at low temperatures and needles when precipitation takes place at high temperatures. The needles tend to align themselves along certain planes in the matrix and to coalesce into plate-like structures. The two phases were found to be related so that a {111} plane and [011] direction of the precipitate are parallel to a {011} plane and [111] direction of the matrix.

DISCUSSION

(*E. A. Anderson presiding*)

D. W. Smith, Pittsburgh, Pa. (written discussion).—This report by Dr. Marzke covers completely all possible heat treatments over a considerable range of compositions in which alpha precipitates from beta brass, and may be said to complete the metallographic part of this problem.

The lining up of needles of segregate to form plates, especially as shown in Fig. 5, appears to be regular, although the author's frequency plot in Fig. 11 makes it appear rather irregular. Has the author attempted any correlation between some of the major directions and the orientation of the parent grain as determined by X-ray analysis? Also, in Figs. 4, 5 and 6 the cross-sections of the needles appear to be straightsided and regular. Have these directions been correlated with the matrix lattice?

Dr. Marzke's method of interpretation of the orientation relationships between the alpha and beta phases is a bit uncertain and seems to need more explanation. If this relationship, as stated, is such that a {111} plane and a [110] direction of that plane in the precipitate is parallel to a {110} plane and a [111] direction of that plane in the matrix, there will be a maximum of 24 possible orientations of the alpha phase within a single grain of the beta phase. This relationship is expressed stereographically in Fig. 13, in which the locations of all of the alpha {111} poles for the 24 orientations of alpha are given. Fig. 12 checks fairly closely with this theoretical plot, with a few exceptions which may be due to the inaccuracy inherent in the method used by the author in determining the orientations of the segregates. The method might have been refined somewhat had corrections been made for the displacement of the slip planes upon deformation.

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* This paper is available at the office of the Institute as *Contribution No.* 29.

AMERICAN INSTITUTE OF MINING AND METALLURGICAL ENGINEERS
Contribution No. 29 (Class E, Institute of Metals Division), February, 1933

DISCUSSION OF THIS PAPER IS INVITED. It should preferably be presented at the New York Meeting, February, 1933, when an abstract of the paper will be read. If this is impossible, discussion in writing may be sent to the Editor, American Institute of Mining and Metallurgical Engineers, 29 West 39th Street, New York, N. Y., for presentation by the Secretary or other representative of its author. Unless special arrangement is made, the discussion of this paper will close April 1, 1933. Any discussion offered thereafter should preferably be in the form of a new paper.

Precipitation of Alpha from Beta Brass*

By Oscar T. Marzke, Lansing, Mich.

(New York Meeting, February, 1933)

Studies on the precipitation of a face-centered from a body-centered structure—a common occurrence in alloy systems—are essential to the development of a theory for the formation of segregate structures. The separation of the alpha phase from the beta of the copper-zinc system is an example of this type of precipitation.

Earlier Studies on the Subject

R. F. Mehl and O. T. Marzke[1] in 1931 presented a paper giving the results of some investigations carried out by them on the segregate structures produced when the alpha and gamma phases of the copper-zinc system and the alpha phase of the copper-aluminum system precipitate from the beta phases of these systems. They showed that the alpha phase precipitates as needles close to the [111] directions of the beta phase. In the discussion of that paper some doubt was expressed about the nature of the segregate. More investigations were undertaken to determine the character of the precipitate in the copper-zinc system and also the orientation relationship between the matrix and precipitate. The present paper gives the results of these investigations.

Since the publication of the earlier paper, several other papers on this subject have been published in this country and abroad. Haneman and Schröder[2] reported that the alpha phase precipitates as needles along the [111] directions of the beta phase and that these needles align themselves to form plates on the {111} planes of the matrix. Mathewson and Smith[3] pointed out that the {111} plane does not contain the [111] direction and that it would be quite impossible, therefore, for needles in the [111] direction to form plates on the {111} plane. They suggested

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* Presented in partial fulfillment of the requirements for the degree of Doctor of Science in Metallurgy, Massachusetts Institute of Technology.

[1] R. F. Mehl and O. T. Marzke: Studies Upon the Widmanstätten Structure, II.—The Beta Copper-zinc Alloys and the Beta Copper-aluminum Alloys. *Trans.* A.I.M.E. (1931) **93,** Inst. of Metals Div., 123.

[2] H. Haneman and O. Schröder: Über die Entstehung und Ausbildungsform von Segregaten in metallischen Mischkristallen. *Ztsch. f. Metallkunde* (1931) **23,** 269.

[3] C. H. Mathewson and D. W. Smith: On the Theory of Formation of Segregate Structures in Alloys. *Trans.* A.I.M.E. (1932) **99,** 264.

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that the plane of precipitation might be the {112}, which was suggested first by A. J. Phillips[4] in discussion of the original paper.

Weerts[5] found that the precipitate in specimens that had been rapidly quenched and then reheated for a short time at a low temperature is in the form of plates parallel to the {011} planes of the matrix, but that the precipitate that separates out at high temperatures is in the form of irregularly outlined needles, which are approximately parallel when of similar orientation. He also found that the orientation relationship between the two phases is regular and independent of the kind of treatment of the specimen, that a {111} plane of the alpha phase is parallel to a {011} of the beta and a [011] direction of the alpha parallel to a [111] of the beta, and that the transformation may be brought about by two simple shifts combined with small changes in dimensions of the unit cells.

The work of D. W. Smith[6] on the precipitation of the alpha phases from the beta of the copper-tin and silver-zinc systems should be mentioned because of the structural analogies between these systems and the copper-zinc. Smith found that the alpha phases precipitate from the beta as needles parallel to the [111] directions of the beta phases and that in the copper-tin system a {111} plane of the alpha phase is parallel to a {011} plane of the beta.

PRESENT INVESTIGATIONS

Preparation and Heat Treatment of Alloys

Preparation.—Alloys of 62, 60, 58 and 56 per cent copper were made from high-purity 60:40 brass, high-purity zinc and doubly electrolyzed copper, furnished by the Chase Brass, New Jersey Zinc, and the United States Metals Refining companies. The alloys were melted in a graphite crucible fitted with a graphite cover; the heating was done in a small gas-fired furnace. No flux was used because of the purity of the materials. The brass was first melted down, the copper then added and, finally, the zinc. The melts were stirred with a graphite rod. The casting temperature was kept as low as possible and the casting was done in an iron mold that was coated with a layer of soot. The size of the mold was 1¼ by 1¼ by 12 in. The bars obtained were cleaned, forged down to ⅜ by 1¾ in., annealed 18 hr. at 810° C., water-quenched, analyzed for copper, and cut into pieces ½ by ½ by 5⁄16 in. for the heat-treatment studies. The analyses for the bars were 61.6, 60.4, 58.4, and 56.2 per cent copper.

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[4] A. J. Phillips: Discussion of paper by Mehl and Marzke. Reference of footnote 1.

[5] J. Weerts: Über Umwandlungvorgänge im β-Messing und in β-Silber-zinklegierungen. *Ztsch. f. Metallkunde* (1932) **11**, 265.

[6] D. W. Smith: A Study of Segregate Structures in Copper-tin and Silver-zinc Alloys. A.I.M.E. *Preprint* (1932).

Heat Treatment.—Three general methods of heat treatment were followed: (1) controlled rate of quenching; (2) rapid quenching followed by reheating; and (3) rapid quenching after furnace cooling various amounts below the transformation temperatures. The heating was done in an ordinary electric muffle furnace. The specimens were fitted with wire holders to facilitate handling and were placed on a nickel screen raised about one inch from the bottom of the furnace.

For studying the effect of the quenching rate on the structure, six different quenching mediums were used: tap water, cold air blast, still air, furnace, sand, and oil at 200° C. Before quenching, the alloys were heated as follows: the 61.6 per cent alloy, 2 hr. at 875° C.; the 60.4 per cent alloy, 2 hr. at 825° C.; the 58.4 per cent alloy, 1 hr. at 800° C. and 1 hr. at 725° C. after furnace cooling from 800° C.; the 56.2 per cent alloy, 1 hr. at 800° C. and 1 hr. at 575° C. after furnace cooling from 800° C.

In studying the effect of rapid quenching followed by reheating, specimens that had been water-quenched from the temperatures mentioned above were heated to 500° C. for 3½ hr., to 400° C. for 24 hr., to 300° C. for 24 hr., to 300° C. for one week, to 200° C. for 24 hr. and to 200° C. for one week. The specimens were air-cooled from the reheating temperatures.

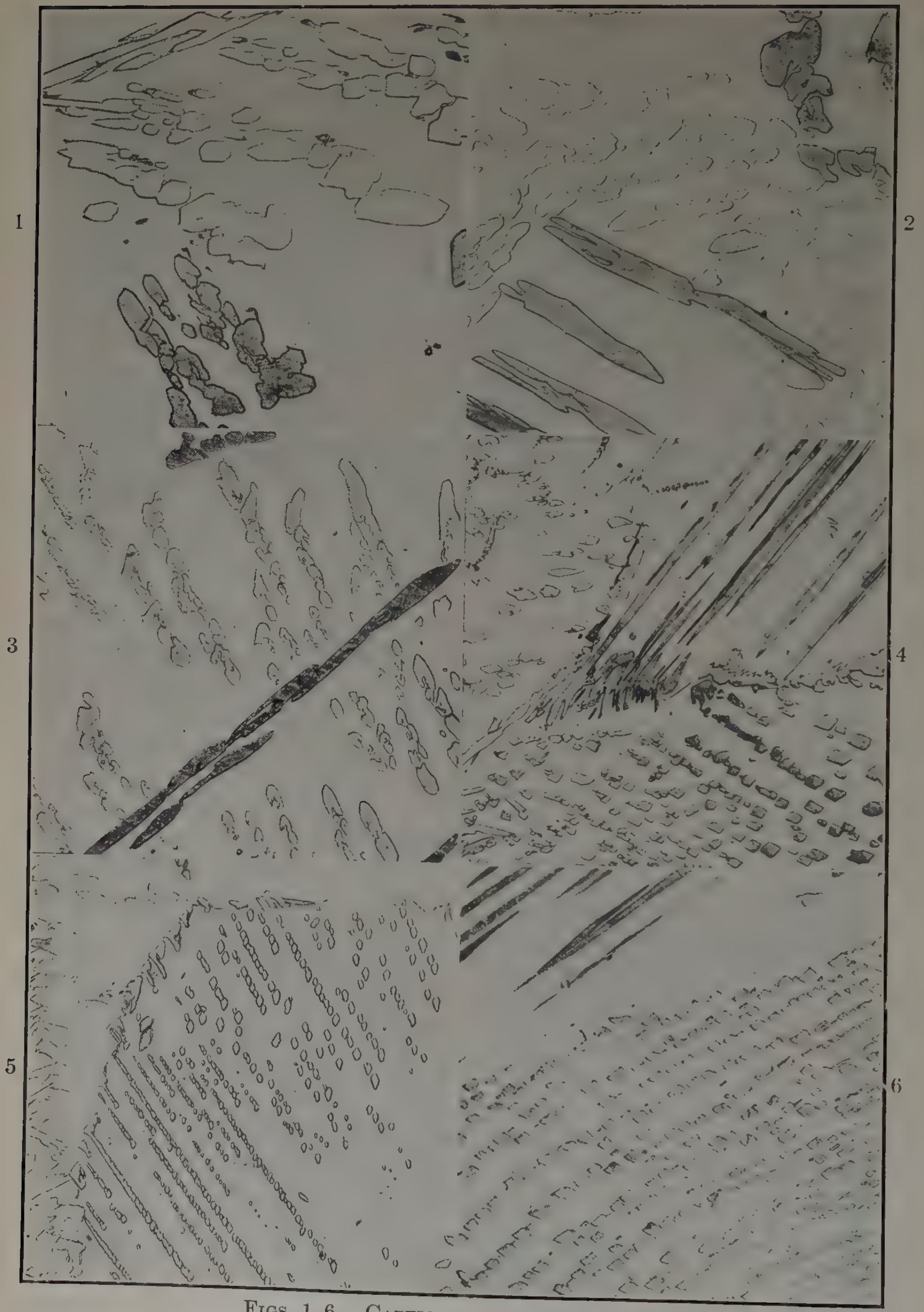
For the last of the heat-treatment studies, specimens of the 61.6 per cent alloy were heated to 870° C. for 2 hr. and water-quenched after furnace cooling to temperatures of 800°, 775°, 750°, 725°, 700°, 650°, 600° and 550° C.; specimens of the 60.4 per cent alloy were heated at 825° C. for 2 hr. and water-quenched after furnace cooling to temperatures of 750°, 725°, 700°, 675°, 650°, 600°, 550° and 500° C.; specimens of the 58.4 per cent alloy were heated to 725° C. for 4 hr. and water-quenched after furnace cooling to temperatures of 675°, 650°, 625°, 580°, 550°, 500° and 450° C.; and specimens of the 56.2 per cent alloy were heated 575° C. for 4 hr. and water-quenched after furnace cooling to temperatures of 500°, 475°, 450°, 425°, 400°, 375°, 350° and 300° C.

Character of Precipitate

All of the specimens were polished, etched and examined under the microscope. A mixture of ammonium hydroxide and hydrogen peroxide was used as the etching reagent.

The specimens from the first and last schemes of heat treatment showed that the alpha phase precipitates as needles. Figs. 1 to 4 exhibit structures found in the four different alloys studied. Two general cross-sections of the segregate are noticed. They are rods and small polygons and may be interpreted as the longitudinal and transverse cross-sections of needles.

Some of the specimens were examined on both sides of an edge formed by two polished faces at approximately 90° to each other. The long



Figs. 1–6.—Captions on opposite page.

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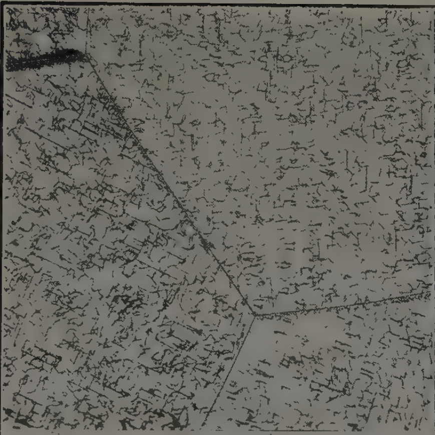

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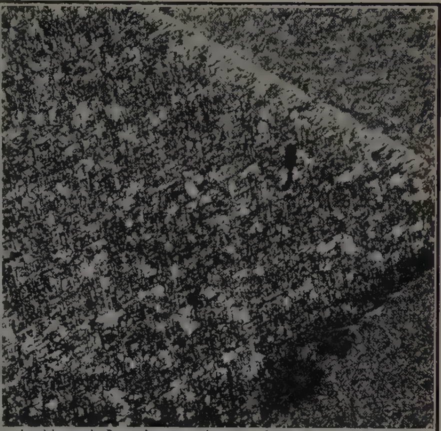

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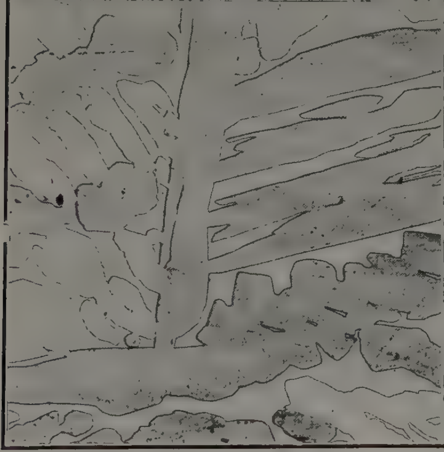

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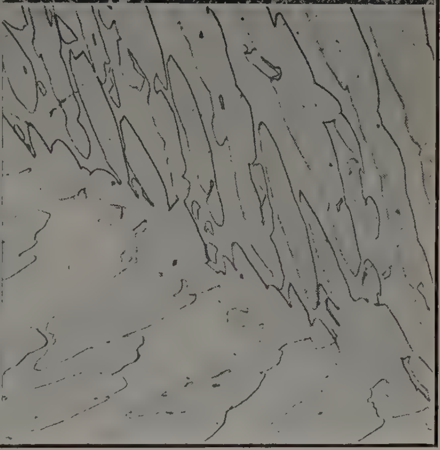

Fig. 7.—58.4 per cent copper. Water-quenched from 725° C. and reheated to 200° C. for 24 hours.
Fig. 8.—60.4 per cent copper. Water-quenched from 825° C. and reheated to 300° C. for 24 hours.
Fig. 9.—61.6 per cent copper. Furnace-cooled from 875° to 550° C. and then water-quenched.
Fig. 10.—60.4 per cent copper. Furnace-cooled from 825° to 600° C. and then water-quenched.
All × 75.

Fig. 1.—61.6 per cent copper. Furnace-cooled from 875° to 800° C. and then water-quenched.
Fig. 2.—60.4 per cent copper. Furnace-cooled from 825° to 725° C. and then water-quenched.
Fig. 3.—58.4 per cent copper. Furnace-cooled from 725° to 650° C. and then water-quenched.
Fig. 4.—56.2 per cent copper. Furnace-cooled from 575° C.
Fig. 5.—56.2 per cent copper. Furnace-cooled from 575° to 475° C. and then water-quenched.
Fig. 6.—56.2 per cent copper. Furnace-cooled from 575° to 425° C. and then water-quenched.
All × 75.

directions of the precipitate on one face generally appeared as dots on the other, which confirmed the needlelike character of the precipitate.

It will be noticed that the small polygons in Figs. 1 to 3 tend to line up along some preferred direction in the matrix. Fig. 5 shows the tendency much better. In this figure the polygons have well defined sides and are aligned so that corresponding sides are parallel and so that one side is parallel to the direction of alignment. This alignment of polygons along certain directions indicates that the needles tend to line up along certain planes in the matrix and may coalesce into platelike structures.

To obtain some idea of the plane along which the needles line up, frequency curves of the directions of the precipitate in several grains were plotted. Grains that showed a marked tendency to give platelike structures were selected for study. Most of the specimens were of the 58.4 per cent alloy because this alloy seemed to give sharper directions than the alloys higher in copper and not such degenerate instances as the alloys lower in copper. Frequency curves of the directions found in five grains are given in Fig. 11. Although certain maxima are indicated, the results are disappointing because of the many scattered directions. Measurements were made of all directions of appreciable size. Sometimes these directions appeared to be the resultant of two or more different directions and in such cases the individual directions were measured rather than the resultant.

These results indicate nothing very definite about the plane of precipitation, unless the rather large number of directions may be taken as proof of a rather irregular grouping of needles into plates. Certain planes, however, do seem to be preferred. In any case, they must be planes containing the direction of the needle.

Dr. Mehl, in a letter to the author, has suggested that the alignment of needles along certain planes may be caused by strains, introduced in the lattice on the precipitation of the first needle, which wedge apart certain planes in the matrix and lead to a high tendency for nuclei formation. The fact that the needles seem to line up on only one plane instead of all of the planes of the same family indicates that there is a greater strain in one direction than in others. This may be due to the manner of matching of atoms between the two phases, which may cause a maximum wedge effect in one direction.

The alignment of needles along certain planes is not general, for many examples were found of needles that were not regularly aligned (Figs. 4 and 6). This irregularity may be due to strains present in the lattice before precipitation occurs, which lead to the formation of many nuclei before one can grow to a needle of sufficient size to strain the lattice preferentially, or to interacting wedge effects from needles not on the same plane.

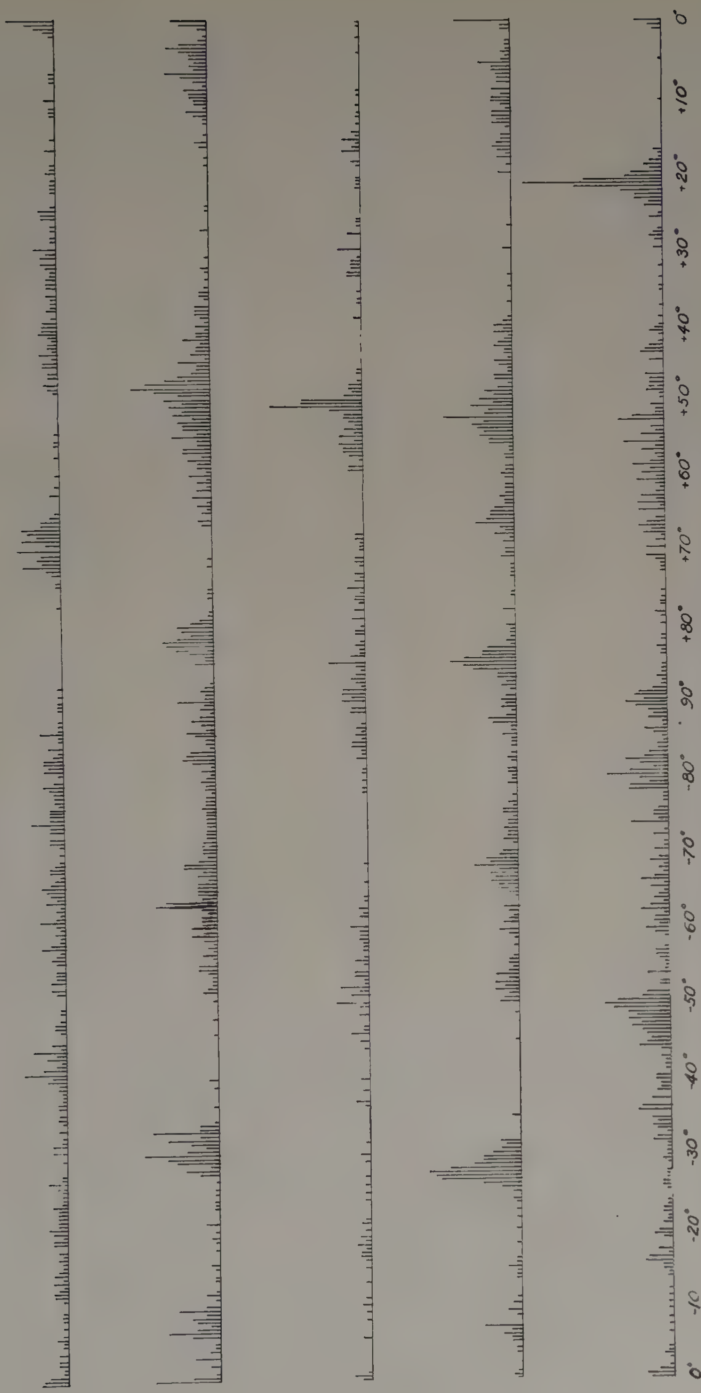

FIG. 11.—FREQUENCY PLOTS OF DIRECTIONS OF TRACES OF PRECIPITATE (ALPHA) IN SEVERAL MATRIX (BETA) GRAINS. THE SHORTEST LINE REPRESENTS ONE TRACE.

The specimens that had been rapidly quenched and then reheated at low temperatures showed that the precipitate may appear as plates (Figs. 7 and 8). A rough examination of Fig. 7 shows six directions of the segregate within a single beta grain, which indicates that the plane of precipitation is the $\{011\}$.

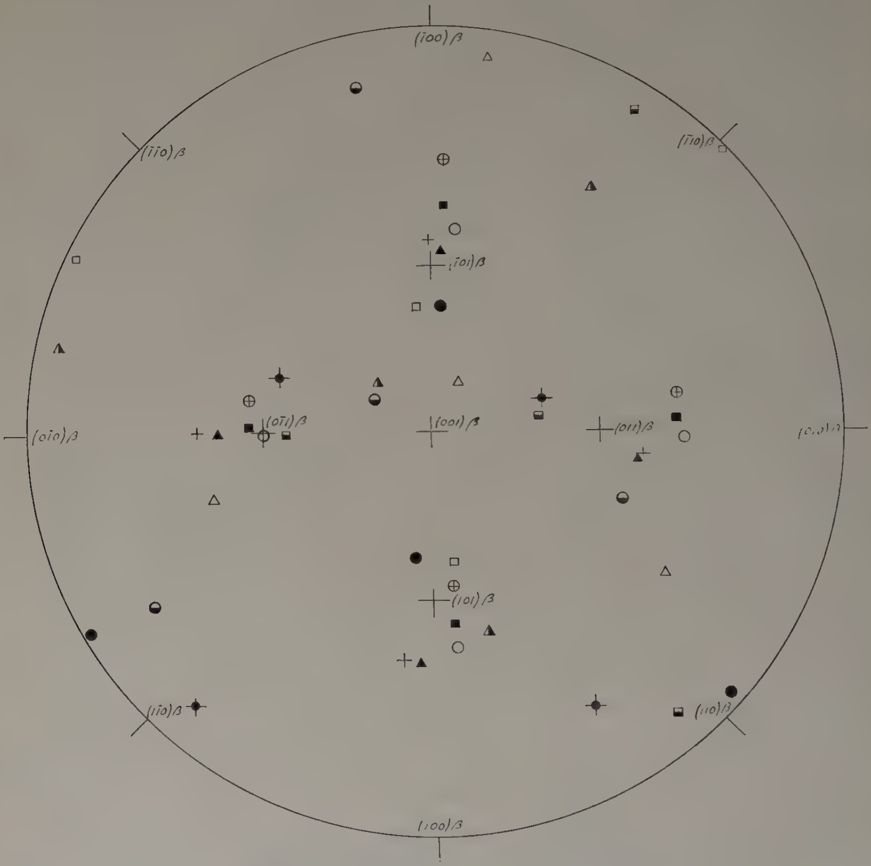

FIG. 12.—POLES OF SEVERAL PRECIPITATE (ALPHA) ORIENTATIONS PLOTTED ON A STANDARD PROJECTION OF THE MATRIX (BETA).

Some of the specimens exhibited structures of particular interest. Fig. 9 shows two precipitate needles of the same orientation making about 65° with each other. This suggests that the long directions in the alpha phase are crystallographic directions making approximately 65° with each other. Fig. 10 shows precipitate of the same orientation in two adjacent grains growing from the same grain boundary. This offers some proof that grain boundaries are not voids or layers of amorphous material but regions where two lattices intersect and share atoms

Relationship in Orientation of the Two Phases

The orientation of the matrix was determined by the Wilson-Davey method.[7] The orientation of the precipitate was found by tracing slip lines around an edge. X-ray methods were avoided because it was felt that the varied orientation of the precipitate would give patterns of great complexity. The most satisfactory slip bands were obtained by compressing a specimen of the 60.4 per cent alloy, polished on two faces, in a Brinell machine under a load of 1000 kg. Twelve precipitate orientations were obtained, representing orientations found in nine different beta grains. These orientations were plotted with the beta orientations so that the {001}, {011} and {111} planes of the precipitate were in the positions they would occupy when the matrix was in the standard position. Stereographic projections were used to express the orientations. The most satisfactory interpretation of these plottings gave a {111} plane and [011] direction of the precipitate parallel to a {011} plane and [111] direction of the matrix. This relationship is shown in Fig. 12. The poor agreement in some of the cases may be explained by the rather large experimental error inherent in the method used.

DISCUSSION OF RESULTS

If the crystal structures of the matrix and precipitate are compared,[8] the best agreement between crystallographic features is found to be between the [111] direction of the matrix and the [011] of the precipitate. The closest agreement between planes is between the {111} of the precipitate and the {011} of the matrix. Since experimental evidence shows that a [111] direction and a {011} plane of the matrix are parallel to a [011] direction and {111} plane of the precipitate, it seems that the orientation relationship between the phases is determined by a close cooperation of the two structures. Such a cooperation has been found, generally, in the other alloy systems studied.

No such explanation can be found for the external appearance of the precipitate. The present study has shown that either plates or needles may result on the precipitation of a face-centered from a body-centered structure, depending on the conditions of precipitation. The needles are formed when the precipitate comes out at a high temperature and the plates when precipitation occurs at a low temperature. At the high temperature the matrix is supposed to have a random arrangement of the atoms and at the low temperature the CsCl structure. It does not seem that this difference in atomic arrangement is responsible for the difference in the character of the precipitate, because plates are found on precipitation from a phase having a random distribution of atoms—meteorites, for example. It does seem, however, that the growth laws of the precipitate are important. At low temperatures the rate of nuclei formation is high, while at high temperatures the growth velocity is great, as shown by the very fine structures obtained at the low temperatures and the coarse structures at the high temperatures. Since the precipitate must grow in a restraining medium, the needles that are formed at the high temperatures may grow because the matrix may permit a more rapid growth in one direction.

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[7] T. A. Wilson: A Study of Crystal Structure and Its Application, XII. *Gen. Elec. Rev.* (1928) **31,** 612.

[8] R. F. Mehl and O. T. Marzke: Reference of footnote 1, Tables 3 and 4.

SUMMARY

1. Alloys of 61.6, 60.4, 58.4 and 56.2 per cent copper were heat-treated in various ways and then examined to find out the effect of these treatments on the character of the precipitate.

2. Two types of precipitate were observed—needles when precipitation takes place at high temperatures, and plates when precipitation occurs at low temperatures.

3. The two phases were found to be related so that a {111} plane and [011] direction of the precipitate are parallel to a {011} plane and [111] direction of the matrix.

ACKNOWLEDGMENT

The author wishes to express his appreciation for the valuable assistance given by Dr. R. F. Mehl and Dr. C. S. Barrett, of the Carnegie Institute of Technology, and Dr. R. S. Williams, of the Massachusetts Institute of Technology.

Fig. 9 shows two segregate needles of the same orientation making an angle of approximately 65° with each other. If the orientation relationship as stated in the above paragraph is to be accepted, we must postulate a secondary growth direction, because it can be shown that segregates growing along two different beta [111] directions cannot have identical orientations.

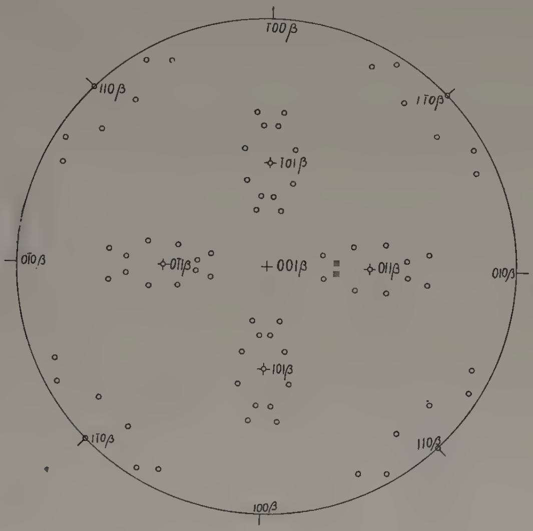

Fig. 13.

C. H. Mathewson, New Haven, Conn. (written discussion).—Kurdjumow and Sachs have proposed as a mechanism for the formation of martensite from austenite a specific shear on a {110} plane and then another on a {112} plane (normal to the first plane), movements which are competent to transform the face-centered cubic lattice of austenite into the body-centered tetragonal lattice of martensite (or the body-centered cubic lattice of alpha iron), when followed by a certain slight adjustment of the atoms to the desired end position.

This change substitutes a {110} plane and [111] direction of martensite or alpha iron for a {111} plane and [110] direction of austenite, which constitutes the relationship of orientation actually found by a complete X-ray structure analysis of the phases.

Obviously, this mechanism may be considered to operate in the reverse direction to account for the occurrence of a {111} plane and [110] direction in alpha brass occupying the positions of a {110} plane and [111] direction in the parent solid solution, beta, as found by Marzke in this investigation and reported by Weerts in the earlier paper quoted by Marzke.

This analogy would indicate the possible occurrence of an intermediate (metastable) phase like the martensite of the iron-carbon system or the beta prime of the copper-aluminum system, although conditions in this respect would depend much upon the lattice dimensions concerned.

The structures of some of the quenched specimens are rather similar to certain ones observed by Smith and Lindlief in their exhaustive microstructural study[1] of the beta transformation in the copper-aluminum alloy containing 11.87 per cent Al; *e. g.*, Fig. 7 (Marzke) to Fig. 32 (S. and L.) and Fig. 8 (Marzke) to Fig. 23 (S. and L.).

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[1] See page 69, this volume.

The double shear mechanism proposed might reveal the locations of both shear planes in the outward form of the segregated alpha, at least in the early stages of its existence. It is apparent from Marzke's work that there is considerable variation in the form of the precipitate. The plates, formed at low temperatures, lie parallel to the {110} plane as this hypothetical mechanism requires, and it is, of course, not impossible that the needles are narrow plates parallel to this plane with another boundary surface parallel to the hypothetical second shear plane, {112}.

M. J. Buerger, Cambridge, Mass.—The number of directions is going to depend on the crystal system of beta brass, and beta brass, as Dr. Marzke would agree after examining some in reflected polarized light, is not cubic, which is unfortunate, so that will cut down the total number of directions and planes that are identical. It is anisotropic; therefore it is at least tetragonal.

A. St. John, New York, N. Y.—Is it necessary to postulate shears of this sort? In some theoretical investigations on transformations between alpha and gamma iron that paralleled a similar theoretical investigation by Bain on martensite and austenite,[2] it was shown that the transformation from one to the other can take place as a simple translation; that is, a compression along two axes and an expansion along the third, or vice versa.[3]

It might seem that this is just what has been referred to; namely, two shears at right angles to each other. But from the point of view of an inhabitant of one of the atoms, it is not. This, by the way, is an excellent point of view to assume if you want to find out what is going on within a crystal. Imagine yourself, for instance, sitting down on a zinc atom in a beta brass crystal, and see how the neighboring copper and zinc atoms look. Then think of some agitations taking place, or some transformation, and see how they behave. The analysis becomes surprisingly simple because there are comparatively few places where neighbors can come to rest and be at ease. Otherwise they are very much agitated. In fact, our heat theory says they are more or less agitated all the time.

A shear involves the slipping of an entire plane of atoms past a neighboring plane to a new position of equilibrium. The transformation by compression and expansion involves a shifting of equilibrium positions and an accompanying displacement of all the atoms. The compression and expansion idea works out well when we think of beta brass in the tetragonal system, for this is the system in which alpha and gamma iron are special cases. Body-centered cubic and face-centered cubic arrangements both appear as special cases in the face-centered tetragonal system, and also in the body-centered tetragonal.

Applying this line of reasoning to the problem of beta brass might lead to elucidation, although I can see complexities introduced by the fact that we have intermixed lattices of zinc and copper.

R. F. Mehl, Pittsburgh, Pa.—The matching of lattice planes and directions in the transformation $\gamma \rightarrow \alpha$ in the iron-carbon system, or in pure iron (in which a body-centered cubic lattice forms from a face-centered cubic lattice), may be described crystallographically as follows:

$$(111)\gamma \| (011)\alpha$$
$$[110]\gamma \| [11\bar{1}]\alpha$$

Since there are three $[110]\gamma$ directions in each $(111)\gamma$ plane and two $[111]\alpha$ directions in each $(011)\alpha$ plane, a total of six orientations of α can, and does, form on each $(111)\gamma$ plane; and since there are four $(111)\gamma$ planes, a grand total of 24 alpha orientations results from the decomposition of each gamma crystal. A stereographic plotting of the orientations resulting from the prescription given proves this.

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[2] K. Heindlhofer and E. C. Bain: Study of the Grain Structure of Martensite. *Trans.* Amer. Soc. Steel Treat. (1930) **18,** 673.

[3] E. C. Bain: Nature of Martensite. *Trans.* A. I. M. E. (1924) **70,** 25.

For the reverse case, in which a face-centered cubic lattice forms from a body-centered cubic lattice, which is studied by Dr. Marzke, the crystallographic specification is the same as that written above, but with reversed directions:

$$(110)\beta \| (111)\alpha$$
$$[111]\beta \| [110]\alpha$$

But following a course of reasoning similar to that above leads to an erroneous conclusion. This reasoning would demand six orientations upon each $(110)\beta$ plane, and since there are six $(110)\beta$ planes, a total of 36 orientations. It may be shown, however, by plotting these orientations stereographically, that only 24 different orientations can result; and an inspection of the six orientations superimposed on a single $(110)\beta$ plane shows that some are identical (which is not true for the reversed case) and that only four are unique on each $(110)\beta$ plane. This is surprising but undoubtedly true. In problems of this sort the stereographic projection is very necessary in avoiding confusion and error.

O. T. Marzke (written discussion).—The importance of using stereographic projections to plot results when working with problems of an involved crystallographic nature is well pointed out by Dr. Mehl.

Attempts were made to correlate the direction of alignment of segregate needles to form plates and the bounding planes of the regularly outlined needles, such as shown in Fig. 5, with the orientation of the matrix, as asked by Dr. Smith, but these attempts were not successful because the grains showing the regularities were generally so small that their orientations could not be determined by the X-ray means used. The method of deducing the plane of precipitation by counting the number of traces in a single matrix grain was not applicable because the cases were generally so degenerate that only one or two directions of alignment were present.

The author agrees with Dr. Smith that the orientation relationship postulated permits a maximum of 24 orientations of the alpha phase within a single grain of the beta phase. In order to determine this relationship, however, it is not necessary to obtain poles for all 24 orientations. In the method used the orientation of an individual alpha particle was completely determined and then plotted with that of the beta to obtain the relationship. The majority of the alpha orientations checked very closely the theoretical positions for the relationship mentioned, closer than for any other relationship investigated. Some of the orientations deviated to a considerable extent, but it was felt that the deviations resulted from the method of determining the orientations of the alpha phase. Dr. Smith's suggestion of refining the method by correcting for the deformation is a good one, but it would be quite difficult to determine the corrections necessary.

If the orientation relationship mentioned is correct and if the two segregate needles in Fig. 9 that make approximately 65° with each other have the same orientation, a secondary growth direction must be postulated, as suggested by Dr. Smith. The fact that when two alpha needles of different orientation, making about 70° with each other, are in the plane of polish, suggesting that they are [111] directions and that a $\{011\}$ plane of the matrix is in the plane of polish, very often a second pair is found which makes an angle of about 10° with the first, and the fact that this second pair of needles etches in such a way that the needles 60° apart etch alike suggests that the alpha phase may grow in a sort of dendritic manner with one arm parallel to a [111] direction of the matrix and another arm growing out from the first, so that the long directions in the precipitate would be the [011]. This would mean that alpha that has precipitated can influence the growth of alpha that is being precipitated, with the result that the direction of some of the precipitate needles may bear no specific relation with any definite crystallographic direction of the matrix.

If the beta phase transforms into the alpha phase by the reverse mechanism of the transformation of austenite into martensite proposed by Kurdjumow and Sachs, the occurrence of an intermediate phase like martensite would be expected, as suggested by Dr. Mathewson. Several X-ray films were made of specimens subjected to heat treatments that, it was thought, would yield this intermediate phase, but all of the results indicated the absence of any such phase. The matrix, however, did appear anisotropic in reflected polarized light, as Dr. Buerger says, indicating that the phase is not isometric. Perhaps more careful X-ray studies will reveal the presence of an intermediate phase.

A little support is offered Dr. Mathewson's suggestion that the needles are narrow plates parallel to the {110} lane with another boundary surface parallel to the {112} plane by the fact that the angle between the sides of the needles aligning to form plates, as shown in Fig. 5, is about 20°, which is approximately that between the (110) and (112) planes.

The mechanism of the transformation proposed by Dr. St. John, if the author understands it correctly, will allow at the most three orientations of the alpha phase. Most of the structures examined indicated more than three orientations, and the X-ray work of Weerts showed that there are 24 alpha orientations in a single beta grain. Furthermore, the mechanism proposed by Dr. St. John requires that an [001] direction of the alpha phase be coincident with an [001] of the beta. In the cases studied by the author there was usually an appreciable angle between these directions; and such an angle is found also in the work of Weerts.

A Micrographic Study of the Decomposition of the β Phase in the Copper-aluminum System*

By Cyril Stanley Smith* and W. Earl Lindlief,* Waterbury, Conn.

(New York Meeting, February, 1933)

Several investigators, mainly concerned with the mechanical properties of the alloys, have studied the so-called aluminum bronzes after various quenching and reheating treatments. Of these works, perhaps the most complete is that of Bouldoires,[1] who studied changes of length, electrical conductivity, thermoelectric force, hardness and microstructure on tempering quenched alloys containing 5 to 20 per cent of aluminum, although the work of Carpenter and Edwards,[2] Curry,[3] Greenwood,[4] Braesco,[5] Matsuda,[6,7] Grard[8] and others has added much to our knowledge of the changes occurring during tempering. The so-called acicular β decomposes on tempering at temperatures between 350° C. and the eutectoid, giving rise to a Widmanstätten structure of α needles in a matrix of δ or fine $\alpha + \delta$, associated with an increase in hardness and almost complete loss of ductility.

Matsuda studied the eutectoid transformation by means of dilatation and electrical conductivity measurements during cooling at different rates. He found that on cooling at the rate of 10° C. per minute there was a decrease in electrical resistance and in length instead of the usual increase which occurred with slow rates of cooling. On tempering the rapidly cooled samples, the increase commenced at about 400° C. and at 520° C. the resistance and length had reached the equilibrium values. These peculiarities he accounted for as being due to a transitional phase β' being formed, β' having an electrical resistance and volume less than either β or $\alpha + \delta$.

Obinata[9] published some electrical conductivity curves for copper-aluminum alloys showing a double break at the eutectoid temperature, which he interpreted as showing the eutectoid change to take place even under equilibrium conditions in two stages, $\beta \rightleftharpoons \beta' \rightleftharpoons \alpha + \delta$, and found that after cooling at critical rates the second phase, showing no acicular markings on etching, could be obtained almost pure. Water quenching was too fast to permit this change to take place completely, and the customary acicular structure was supposed to be a $\beta - \beta'$ complex. He determined the crystal structure of the β' phase obtained by quenching, and found it to be hexagonal, compared with the body-centered cubic form for β at high temperatures. The critically cooled β' phase was found to be much harder than any other condition of the eutectoid alloy. Obinata's work will be discussed later in connection with the findings of the present authors, who discovered microscopically a transitional β' phase probably identical with that of Obinata, although it is not an equilibrium constituent and is not harder than acicular β.

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* Copper Alloys Research Laboratory, The American Brass Co.

[1] J. Bouldoires: *Rev. de. Mét.* (1927) **24,** 357 and 463.

[2] H. C. H. Carpenter and C. A. Edwards: *Proc.* Inst. Mech. Engrs. (1907) **57.**

[3] B. E. Curry: *Jnl. Phys. Chem.* (1907) **11,** 423.

[4] J. M. Greenwood: *Jnl.* Inst. Metals (1918) **19,** 55.

[5] P. Braesco: *Ann. Phys.* [9] (1920) **14,** 5.

[6] M. Matsuda: *Sci. Repts.* Tohoku Imp. Univ. (1922) **11,** 234.

[7] M. Matsuda: *Jnl.* Inst. Metals (1928) **39,** 67.

[8] C. Grard: Aluminum and Its Alloys, Pt. V. New York, 1922. D. Van Nostrand Co.

[9] I. Obinata: *Mem.* Ryojun Coll. Eng. (1928–30) **2,** 205; (1929–31) **3,** 87, 285, 295.

The present work is a discussion of the mechanism of transformation at various temperatures below the eutectoid point, the transformation temperature being approached directly from the β field without intermediate cooling below. In the elimination of the prior quenching the method is quite different from the early tempering experiments and permits the mechanism of transformation on cooling to be better understood. The method of attack was suggested by the work of Davenport and Bain[10] on the transformation of austenite at constant subcritical temperatures.

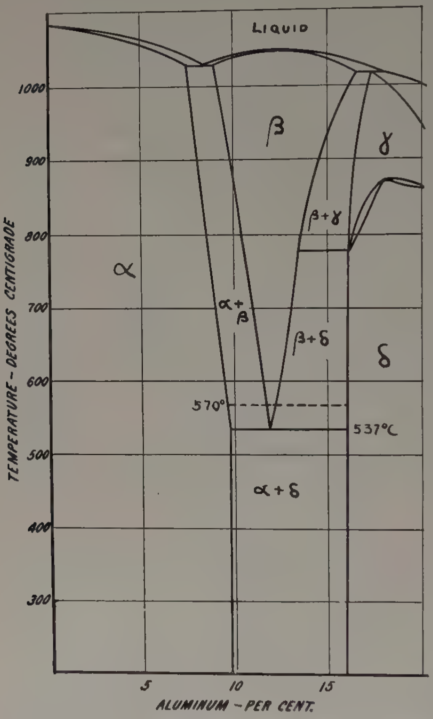

FIG. 1.—COPPER-ALUMINUM EQUILIBRIUM DIAGRAM. (*Stockdale; slightly modified.*)

REDETERMINATION OF EUTECTOID TEMPERATURE

Fig. 1 shows the copper-rich portion of the copper-aluminum equilibrium diagram, slightly modified from that of Stockdale.[11,12] The diagrams proposed by other investigators agree in showing a eutectoid at about 11.9 per cent aluminum, but the various determinations of the eutectoid temperature differ widely. Table 1 lists several of the values published and the methods used in obtaining them. The temperatures obtained by the different observers on heating agree much better than do the cooling-curve points, and the discrepancy is probably due to variations of cooling rate.

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[10] E. S. Davenport and E. C. Bain: *Trans.* A.I.M.E. (1930) **90,** Iron and Steel Div., 117.

[11] D. Stockdale: *Jnl.* Inst. Metals (1922) **28,** 273.

[12] D. Stockdale: *Jnl.* Inst. Metals (1924) **31,** 275

TABLE 1.—*Eutectoid Temperature of the Copper-aluminum System*

Year	Investigators	Reference No.	Method	Eutectoid Temperature, Deg. C.
1907	Carpenter and Edwards	2	Thermal analysis	530, 520
1907	Curry	3	Thermal analysis	566
1915	Andrew	13	Thermal analysis	515
1915	Carpenter	14	Critical review	545
1920	Braesco	5	Dilatation	550–560
1922	Stockdale	11, 12	Annealing	537
1922	Ishihara	15	Hardness	565
1922	Matsuda	6, 7	Micro, dilatation, elec. cond., etc.	560–570
1927	Bouldoires	1	Dilatation, elec. cond., etc.	560
1929	Obinata	9	Electrical conductivity	590, 600

To decide between the many temperatures proposed, the authors carried out some further experiments using both microscopic and electrical resistance methods. A series of annealing and quenching experiments were carried out, using a single alloy (alloy 577) of the following analysis: copper, 88.04 per cent; aluminum, 11.87 (by diff., 11.83 by det.); iron, 0.06; silicon, 0.02; tin, 0.01; lead, 0.00; manganese, 0.00. The spectrograph showed the presence of no elements other than those in this analysis.

Two samples were used for the anneal at each temperature: one consisting entirely of eutectoid, having been previously very slowly cooled from 900° C. to room temperature; and the other consisting of homogeneous β, having been annealed for 1 hr. at 900° C. and then put directly in the salt bath at the desired temperature without intermediate cooling below. In this manner the transformation point was approached from both sides and the effect of undercooling or superheating eliminated.

The two samples (eutectoid and homogeneous β) were placed in a salt bath maintained within ±1° C. of the desired temperature and quenched in water after a given period of time. The annealings at 568° and 572° C. were done in a furnace with more accurate control. Micro-

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[13] J. H. Andrew: *Jnl.* Inst. Metals (1915) **13,** 249.

[14] H. C. H. Carpenter: *Jnl.* Inst. Metals (1915) **13,** 261.

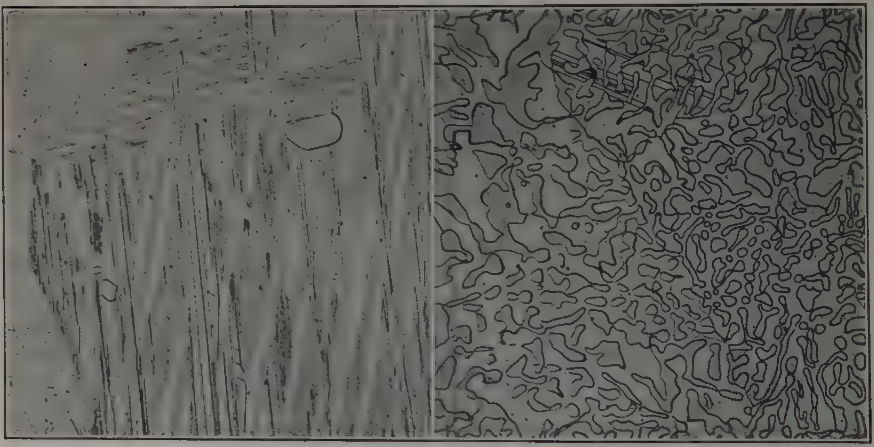
[15] T. Ishihara: *Sci. Repts.* Tohoku Imp. Univ. (1922) **11,** 207.

scopic examination of the samples quenched after the desired time readily showed if the temperature had been above or below that at which the transformation occurs. Table 2 gives the various anneals and corresponding structures.

TABLE 2.—*Microstructure of Samples Annealed in Neighborhood of Eutectoid Temperature*

Temperature, Deg. C.	Time, Hr.	Microstructure	
		Eutectoid Sample	Homogeneous Sample
566	9	Unchanged, $\alpha + \delta$	Eutectoid, $\alpha + \delta$
568 ± 0.5	63	Unchanged, $\alpha + \delta$	Eutectoid, $\alpha + \delta$
570	12	Unchanged, $\alpha + \delta$	β + traces δ
572 ± 0.5	68	β + traces δ	β + traces δ
573	33	β + traces δ	β + traces δ

Evidently the eutectoid transformation occurs at 570 ± 1° C., for both β and eutectoid were unchanged by a 12-hr. anneal at this temperature, while 572° C. was definitely in the β field and 568° C. definitely below the transformation point when approached from either side. Fig. 2 shows the structure of the eutectoid sample annealed at 572° C.; Fig. 3, that of the sample that originally was β, after annealing at 568° C. The composition of the eutectoid apparently is slightly less than 11.87 per cent aluminum, since both samples annealed at 572° C. contained a small quantity of proeutectoid δ.



FIGS. 2 AND 3.—ALLOY 577, CONTAINING 11.87 PER CENT ALUMINUM. ETCHED WITH $NH_4OH + H_2O_2$. × 200.

Fig. 2 annealed 68 hr. at 572° C. and quenched. Originally $\alpha + \delta$.
Fig. 3 annealed 68 hr. at 568° C. and quenched. Originally β.

The transformation temperature was also determined by electrical conductivity measurements. For these a sample approximately 8 by ¼ by ⅛ in. was used, bent into a compact grid and insulated with sheet mica. To obtain the sample in the eutectoid condition prior to taking the heating curve, it was annealed 4 hr. at 800° C., furnace-cooled to 535° C. and held at this temperature for 12 hr., then furnace-cooled to room temperature. The heating curve over the range 50° to 700° C. was taken in a period of 33 hr., the heating rate through the range 560° to 575° C. being about 3° C. an hour. The cooling rate employed was much slower, the time required to take the curve over the range 700° C. to room temperature being seven days. Two days were allowed in the range 573° to 564° C. The results of both heating and cooling curves are shown in Fig. 4, the resistance ordinate being displaced to separate the two curves. The anomaly in the α solid solution discovered by Chevenard[16] shows as a change in slope at 275° C. on heating and 350° C. on cooling. The sharp drop due to the formation of β occurs between 569° and 573° C. on heating, while on cooling the transformation is very sluggish, commencing between 571° and 567° C., but is not more than 60 per cent complete at 565° C. in spite of the very long time allowed between readings at these temperatures.

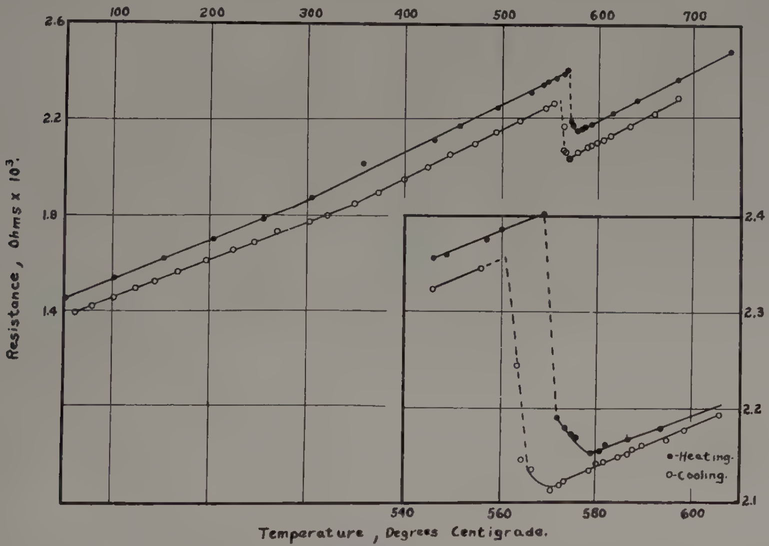


FIG. 4.—ELECTRICAL RESISTANCE TEMPERATURE CURVES OF AN ALUMINUM-COPPER ALLOY CONTAINING 11.87 PER CENT ALUMINUM.

Resistance ordinate displaced to separate heating and cooling curves.

Comparing the microscopic and electrical conductivity measurements, it can be said that the eutectoid temperature is 570° ± 1° C.

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[16] P. Chevenard: *Jnl.* Inst. Metals (1926) **2,** 39; *Compt. rend.* (1925) **180,** 1927.

Obinata[17] gave a resistance curve different from that of the authors in that it showed two breaks instead of one. The first occurred at 590° C. and was followed by an extremely rapid rise up to 600° C. where the second drop occurred, followed by a normal slope due to the temperature coefficient of the β phase. He interpreted the interval between the two breaks as due to a β′ phase of extremely high temperature coefficient, and by quenching at a critical rate, he was able to obtain a substantially homogeneous phase which he determined to be hexagonal in structure. The double break in the resistance curve appeared even on rapid heating, but rapid cooling caused a drop rather than rise in resistance and even on cooling at normal rates (3° to 4° C. per minute) the double break did not appear, but only a single increase in resistance at about 550° to 540° C.

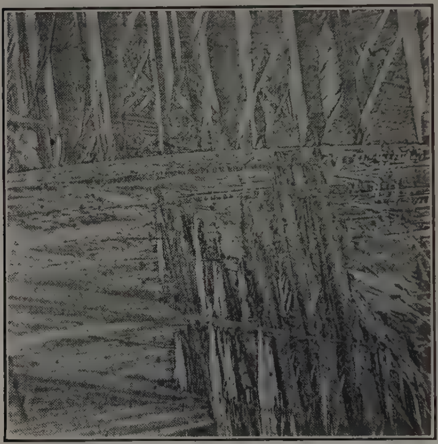

FIG. 5.—ALLOY 577, CONTAINING 11.87 PER CENT ALUMINUM. QUENCHED FROM 900° C. ETCHED WITH $NH_4OH + H_2O_2$. × 250.

DECOMPOSITION OF β PHASE AT TEMPERATURES BELOW EUTECTOID POINT

An extensive study was made of the decomposition of the β phase at various temperatures below the eutectoid point, both by cooling directly, without intermediate cooling to room temperature, and by quenching and reheating to the desired temperature. The alloy used for all these experiments was cast in an ingot measuring 14 by 3½ by 1 in. and was hot-rolled to sheet 0.125 in. thick. It had the composition given on page 71. The study of transformation was done mainly by microscopic methods, the procedure being as follows: A suitable number of small samples of the ⅛-in. sheet were annealed for 1 hr. at 900° C., then quenched directly into a salt bath maintained at the desired temperature. After various periods of time single samples were removed from the salt bath, quenched in ice water and examined microscopically to determine the progress of the transformation.

A sample quenched in water from 900° C. has the characteristic structure, shown in Fig. 5, which is usually called "acicular" β, and probably represents an early stage in the decomposition of the β phase. As Mehl[18] shows, it is improbable that there really exist needles, and many structures called acicular are merely plate-form. β cannot be retained

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[17] I. Obinata: Reference of footnote 9.

[18] R. F. Mehl and O. T. Marzke: *Trans.* A.I.M.E. (1931) **93,** Inst. Met. Div., 123.

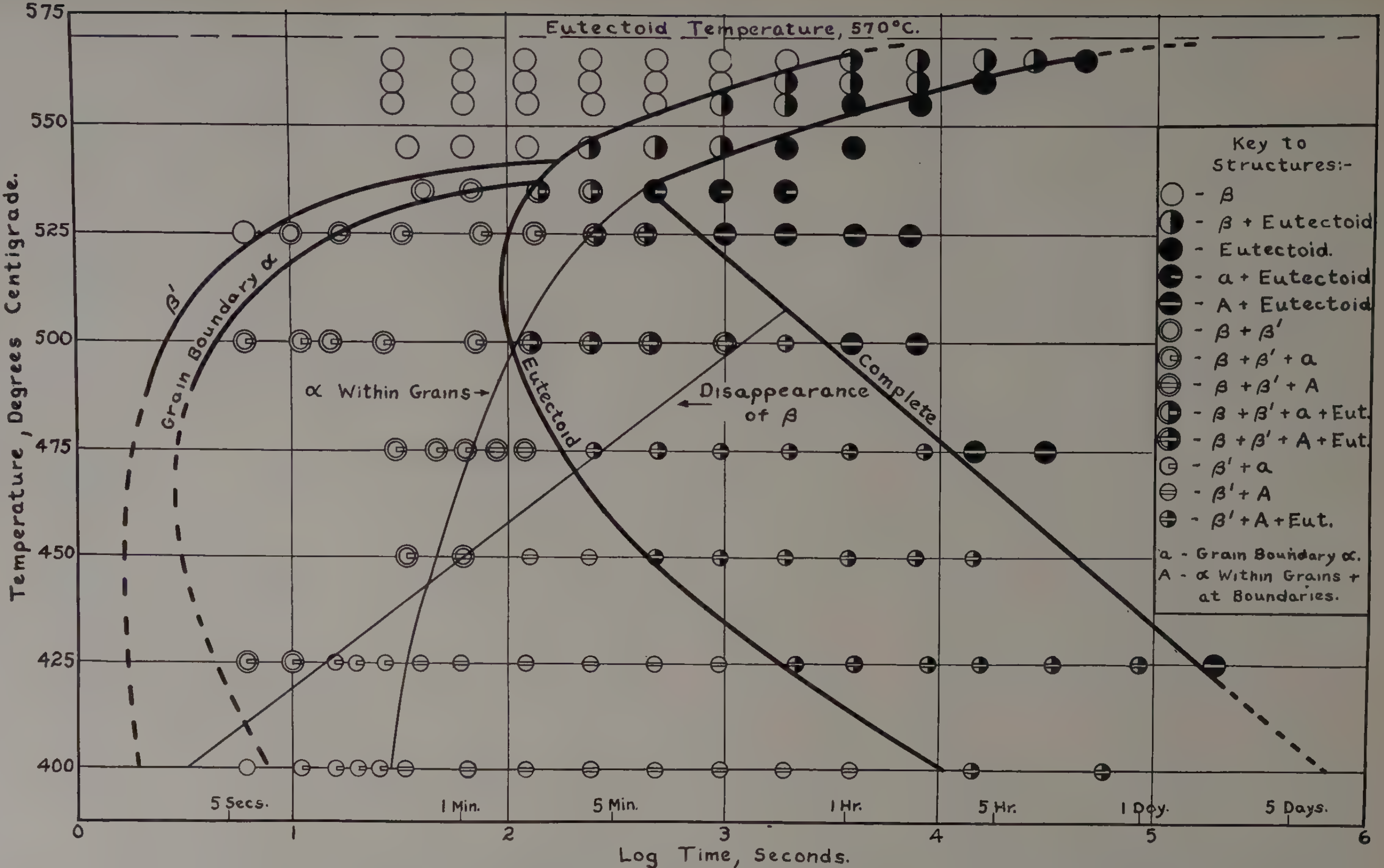

FIG. 6.—TIME OF APPEARANCE OF MICROCONSTITUENTS DURING DECOMPOSITION OF ALUMINUM-COPPER β PHASE OF EUTECTOID COMPOSITION.

TABLE 3.—*Structures Observed in Alloy 577 after Various Periods of Time at Certain Temperatures*

Temperature	565° C.	560° C.	555° C.	545° C.	535° C.	525° C.	500° C.	475° C.	450° C.	425° C.	400° C.	375° C.	350° C.	300° C.
Time[a]						6	6			6	6			
Structure[b]						B	Bb a			Bb a	b			
Hardness[c]						64.1	73.5			66.0	65.0			
Time						10	11			10	11			
Structure						Bb a	Bb a			Bb a	b a			
Hardness						65.9	70.6			64.1	64.5			
Time						17	15			16	16			
Structure						Bb	Bb a			b a	b a			
Hardness						67.3	67.5			64.5	65.7			
Time						20	22			20	20			
Structure						Bb a	Bb a			b a	b a			
Hardness						66.2	69.0			65.2	66.0			
Time						26	26			27	26			
Structure						Bb a	Bb a			b a	b a			
Hardness						68.4	71.4			65.9	67.2			
Time	30	30	30	35	41	32	27	30	34	39	33	60	120	40
Structure	B	B	B	B	Bb	Bb a	Bb a	Bb a	Bb a	b A	b A			
Hardness	67.6	67.8	68.7	68.6	64.8	69.9	74.4	69.8	69.9	70.5	68.7	69.3	67.7	66.9
Time	61	63	61	61	67	75	70	47	62	60	64	120	241	70
Structure	B	B	B	B	Bb	Bb a	Bb a	Bb a	Bb A	b A	b A			
Hardness	67.2	66.7	66.4	67.0	68.7	70.9	73.4	64.2		67.2	70.6	72.6		67.8
Time	121	120	123	123	137	132	126	63	127	120	119	240	482	122
Structure	B	B	B	B	Bb a 0.5% E	Bb a	Bb A tr. E	Bb a	b A	b A	b A			
Hardness	66.8		67.3	67.0	68.8	69.6	72 3	67.5	72.1	71.4	72.9	74.8	70.8	66.3
Time	240	240	243	242	240	250	242	90	240	240	240	480	966	243
Structure	B	B	B	B 0.1% E	Bb a 17.7% E	Bb A 19.0% E	Bb A 2.5% E	Bb A	b A	b A	b A			
Hardness	66.3	66.0	65.0	67.4	69.4	71.2	73.7	64.7	76.4	77.9	77.8	73.4	68.9	67.3
Time	480	481	481	481	480	483	498	120	482	480	480	960	2,040	495
Structure	B	B	B	B 5.0% E	100% E	Bb A 20.2% E	Bb A 12.1% E	Bb A	b A tr. E	b A	b A			
Hardness	64.9	69.1	66.8	66.0	82.9	77.1	79.6	72.1	76.3	79.5	81.7	75.0	67.2	67.9
Time	960	965	961	961	960	975	976	244	960	960	960	1,920	1 hr.+	963
Structure	B	B	B 0.6% E	B 99.8% E	100% E	100% E	Bb A 53.7% E	b A 0.3% E	b A tr. E	b A	b A			
Hardness	66.5	66.6	66.9	80.2	93.3	95.5	84.6	77.7	75.8	79.9	80.9	76.3	69.3	68.4
Time	1,920	1,920	1,920	1,922	1,923	1,922	1,920	485	1,920	2,160	1,920	1 hr.+	2 hr.+	1,862
Structure	B	B 0.1% E	B 36.9% E	100% E	100% E	100% E	b A 85.2% E	b A 1.3% E	b A 3.3% E	b A tr. E	b A			
Hardness	66.4	65.0	67.3	94.1	80.0?	95.5	85.9	76.7	74.9	79.7	84.8	73.0	69.9	67.6

TABLE 3.—(*Continued*)

Temperature	565° F.	560° C.	555° C.	545° C.	535° C.	525° C.	500° C.	475° C.	450° C.	425° C.	400° C.	375° C.	350° C.	300° C
Time..... Structure.. Hardness..	3,840 B 1.8% E 68.4	3,840 B 13.4% E 67.6	3,935 100% E 88.9	3,900 100% E 92.6		4,020 100% E 95.3	3,870 100% E 93.4	963 b A 1.4% E 75.9	3,840 b A 8.2% E 73.7	4,080 b A tr. E 75.1	3,855 b A	2 hr.+ 77.7	4 hr. 71.1	1 hr. 67.7
Time..... Structure.. Hardness..	7,680 B 23.0% E 68.4	7,680 B 99.3% E 77.9	7,920 100% E 89.2			7,250 100% E 96.7	7,810 100% E 92.2	1,980 b A 3.4% E 76.2	7,680 b A 20.6% E 76.6	9,180 b A 0.8% E	14,415 b A tr. E 84.8	4¼ hr. 79.1	8 hr.+ 74.5	2½ hr. 67.9
Time..... Structure.. Hardness..	15,915 B 98.7% E 73.7	15,905 100% E 83.6						3,844 b A 8.4% E 78.3	14,400 b A 43.2% E 80.4	16,020 b A 3.8% E 74.7	59,400 b A 9.3% E 83.0	8¼ hr. 80.0	16 hr. 77.3	49 hr. 72.2
Time..... Structure.. Hardness..	27,000 B 99.4% E 80.9							8,445 b A 65.3% E 80.5		34,200 b A 11.6% E 74.2		22½ hr. 84.4	35 hr. 85.0	
Time..... Structure.. Hardness..	46,800 100% E 82.1							14,940 100% E 85.5		86,400 b A 22.3% E 75.9		46½ hr.	3 days	
Time..... Structure.. Hardness..								30,840 100% E 87.1		194,400 100% E 83.9		7 days 84.1	6 days 88.7	
Time..... Structure.. Hardness..												21 days	12 days 87.4	
Time..... Structure.. Hardness..												32 days	20 days 86.5	

[a] Time in seconds unless otherwise marked.

[b] Structures: B = beta (β).
b = beta prime (β').
a = alpha at grain boundaries. (α)
A = alpha within grains and at grain boundaries.
E = eutectoid. (Below 535° C. the eutectoid contains primary alpha but this phase is not listed separately except in partially transformed samples where it occurs in beta.)
Tr. = trace.

The microstructures at temperatures below 400° C. are difficult to interpret therefore these structures are not listed.

[c] Rockwell hardness, measured by B scale, 1/16-in. ball, 150 kg.

unchanged even by the most drastic quench, although Obinata was able to obtain a partially homogeneous alloy by quenching in toluene at −70° C.

The structures observed after various periods of time at the different temperatures are listed in Table 3. The results are also plotted in Fig. 6, which shows graphically the time of decomposition and the microconstituents formed. In Fig. 7 the relative area of eutectoid formed after various times at several temperatures is shown. The mechanism of transformation at the various temperatures will be considered individually.

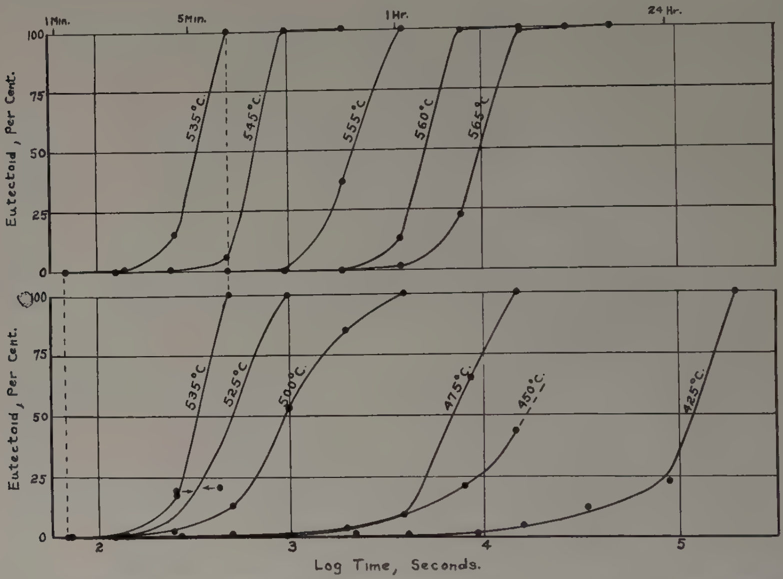

FIG. 7.—PROGRESS OF EUTECTOID TRANSFORMATION AT VARIOUS TEMPERATURES.

Transformations at Various Temperatures

Transformation at 565° *C.*—Samples quenched after short periods of time at 565° C. (only 5° C. below the eutectoid temperature) had acicular structures identical with those of samples directly quenched from a high temperature (cf. Fig. 5). There was no change in structure until the first appearance of eutectoid occurred at 3840 sec. Fig. 8 shows the growth of the eutectoid after 7680 sec. There was very little, if any, relation of

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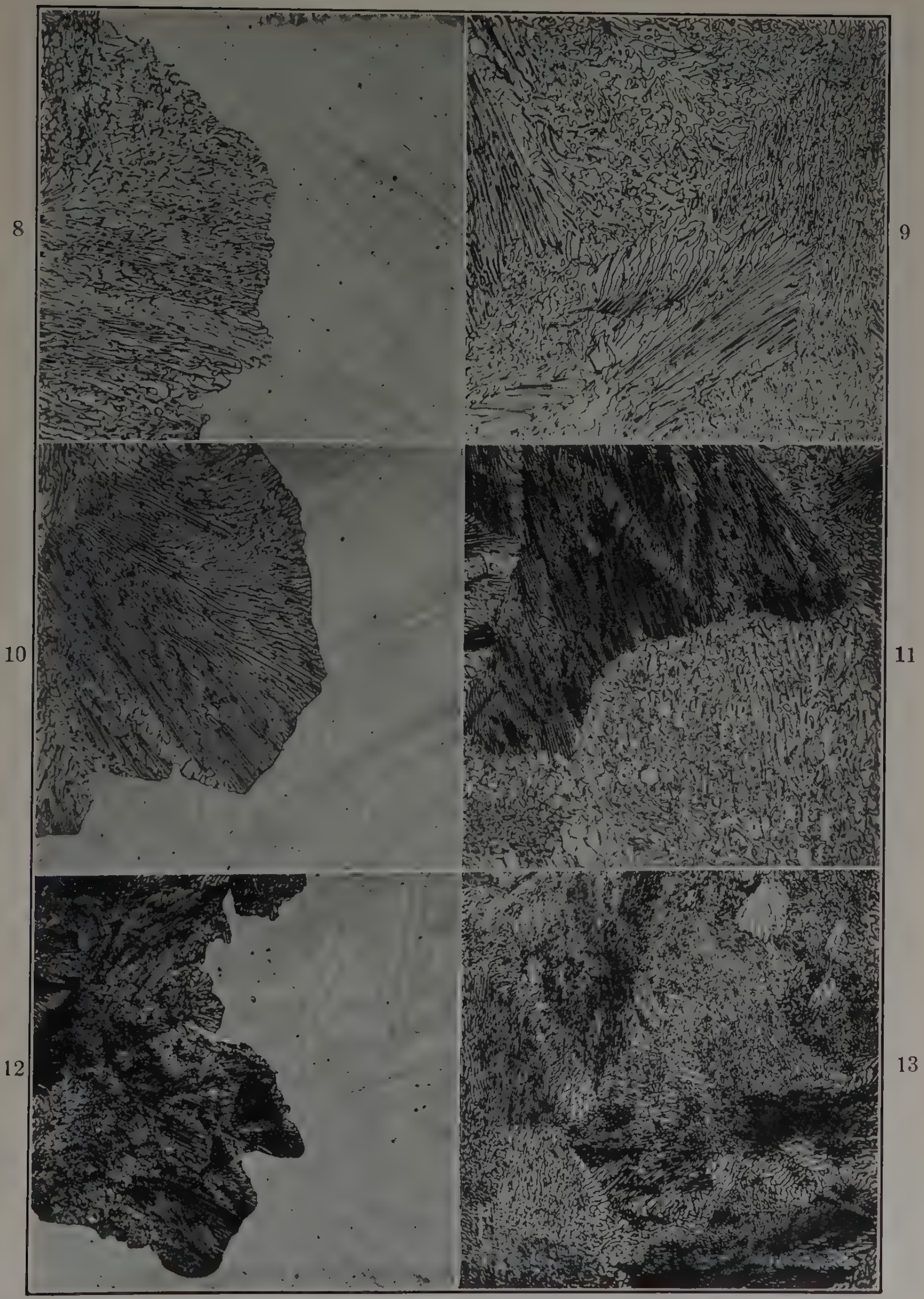
FIGS. 8–13.—ALLOY 577, CONTAINING 11.87 PER CENT ALUMINUM. QUENCHED FROM 900° C. IN SALT BATH AT TEMPERATURE, HELD FOR TIME STATED AND QUENCHED IN ICE WATER. ETCHED WITH $NH_4OH + H_2O_2$.

Fig. 8.—Held at 565° C. 7680 sec. × 250.
Fig. 9.—Held at 565° C. 13 hr. × 200.
Fig. 10.—Held at 560° C. 3840 sec. × 250.
Fig. 11.—Held at 560° C. 4 hr. × 200.
Fig. 12.—Held at 555° C. 1920 sec. × 250.
Fig. 13.—Held at 555° C. 3935 sec. × 200.



Figs. 8–13.—Captions on opposite page.

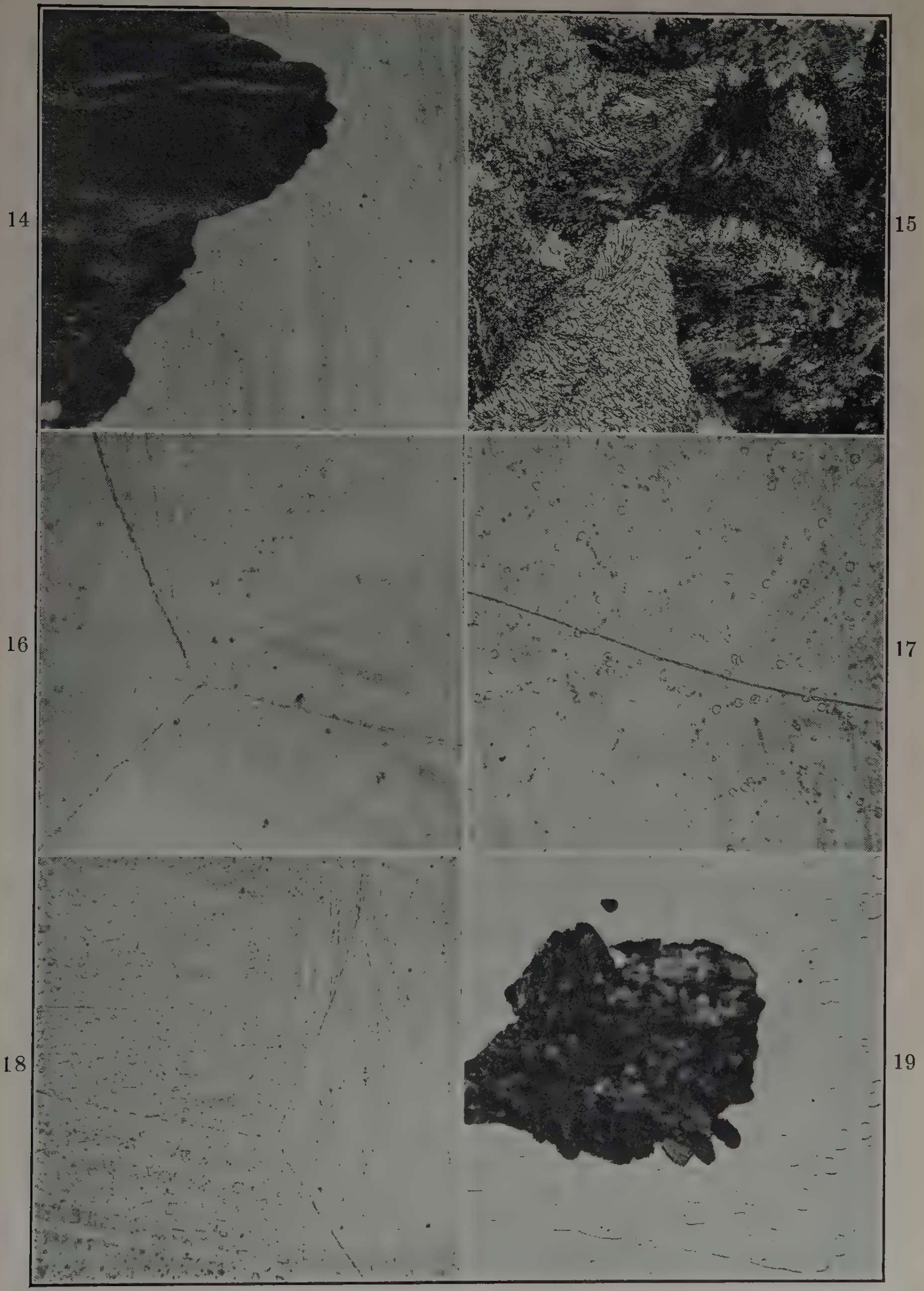
orientation between the eutectoid and the parent crystals. The eutectoid grew preferentially in the direction of the length of the plates, tending to give radial patches of eutectoid. Slip bands in the α constituent in the eutectoid showed it to have the same orientation throughout a large part of a single eutectoid colony. It is probable that δ was also of one orientation only and that the two are related to each other and to the parent β lattice even though the characteristic pseudoidiomorphic Widmanstätten shape is not adopted. The entire sample had changed to eutectoid after 46,800 sec. (15 hr.), as Fig. 9 shows.

Transformation at 560° *to* 545° *C.*—The eutectoid formed in progressively shorter time at lower temperatures and the spacing of the eutectoid plates became finer, otherwise the mechanism was the same as at 565° C. This is shown by Figs. 10 to 15, which are photomicrographs of specimens partially and completely transformed at 560°, 555° and 545° C. respectively.

Transformation at 535° *C.*—At this temperature a remarkable new phase made its appearance in the β before the formation of eutectoid commenced. It occurred even in the first specimen, quenched after 41 sec., and was in the form of small scattered rosette-shaped particles which occurred at random throughout the grains and especially at the boundaries. Fig. 16 shows their appearance at a magnification of 500 in the first specimen; Fig. 17, their growth after 67 sec. at 535° C. As time increased this new phase continued to grow and the martensitic needlelike markings produced by quenching could sometimes be seen to traverse both the original β phase and new phase indiscriminately (Fig. 18). At high magnification many of the particles of the new phase could be seen to have kernels which appeared as black spots, but it is probable that these were alumina or other inclusions existing in the original metal, merely serving as nuclei for precipitation. In the specimen quenched after 137 sec. at 535° C., distinct α crystals could be seen growing in the middle of many of the nodules of the new phase, and one small area of eutectoid was found in the specimen. With longer time, the eutectoid areas increased, growing indiscriminately through the new phase and the unchanged β (Fig. 19). The area occupied by β was progressively absorbed by both the new phase and the eutectoid, but the latter, once formed, grew more rapidly, and the entire specimen was transformed to it after 480 sec. (Fig. 20).

FIGS. 14–19.—ALLOY 577, CONTAINING 11.87 PER CENT ALUMINUM. QUENCHED FROM 900° C. IN SALT BATH AT TEMPERATURE, HELD FOR TIME STATED AND QUENCHED IN ICE WATER. ETCHED WITH $NH_4OH + H_2O_2$.

Fig. 14.—Held at 545° C.	481 sec.	× 250.
Fig. 15.—Held at 545° C.	1922 sec.	× 200.
Fig. 16.—Held at 535° C.	41 sec.	× 500.
Fig. 17.—Held at 535° C.	67 sec.	× 250.
Fig. 18.—Held at 535° C.	137 sec.	× 250.
Fig. 19.—Held at 535° C.	240 sec.	× 500.



Figs. 14–19.—Captions on opposite page.

The etching characteristics of the new phase, its relation in color and marking to β, and the fact that the eutectoid patches grew across both phases with little change, suggested that the new phase was closely related to β in structure. It seems to be a transitional phase, not represented on the equilibrium diagram, produced only by the decomposition of β at certain temperatures. It has been called β' (beta prime) and the mechanism of its formation will be discussed later.

Transformation at 525° *C.*—The first sample, quenched after only 6 sec., was homogeneous β. A little of β' appeared in 10 sec. (Fig. 21) and α appeared after 17 sec. as a very thin film at the grain boundaries only, later growing into the body of the grains. α was always in contact with β' and was never encountered in contact with β directly. Eutectoid appeared in the specimen quenched after 250 sec., and the patches of this rapidly grew and absorbed both the β and β' areas, leaving the α needles embedded in it (Figs. 22 and 23). It is interesting to note that although eutectoid grew indiscriminately through β and β', that which was formed from a β' area was distinctly different in tint from that formed from β. This became more marked the lower the temperature, and indicated a different proportion of aluminum in β', a fact that agrees with the ready crystallization of proeutectoid α from β', which must result in its enrichment with aluminum.

Transformation at 500° *C.*—Transformation at this temperature commenced earlier than at 525° C. An extremely small quantity of α was visible at the grain boundaries even in the sample quenched after 6 sec. After 27 sec. there was about 70 per cent of β' in the body of the grain and an almost continuous layer at the boundaries. It was not until 126 sec. that clearly visible α needles formed within the grains and the first traces of eutectoid became visible at the same time. Figs. 24 and 25 show, at different magnifications, the structure of the specimen quenched after 242 sec. at 525° C. The growth of α was rapid and a considerable proportion of α needles was visible before the β and β' had finally decomposed to eutectoid. β had completely transformed to β' before the last portions had decomposed. Figs. 26 and 27 show two stages in the completion of the transformation at this temperature.

Transformation at 475° *C.*—After only 30 sec. at 475° C., the specimen consisted almost entirely of fine-grained β' (Fig. 28). α was present as

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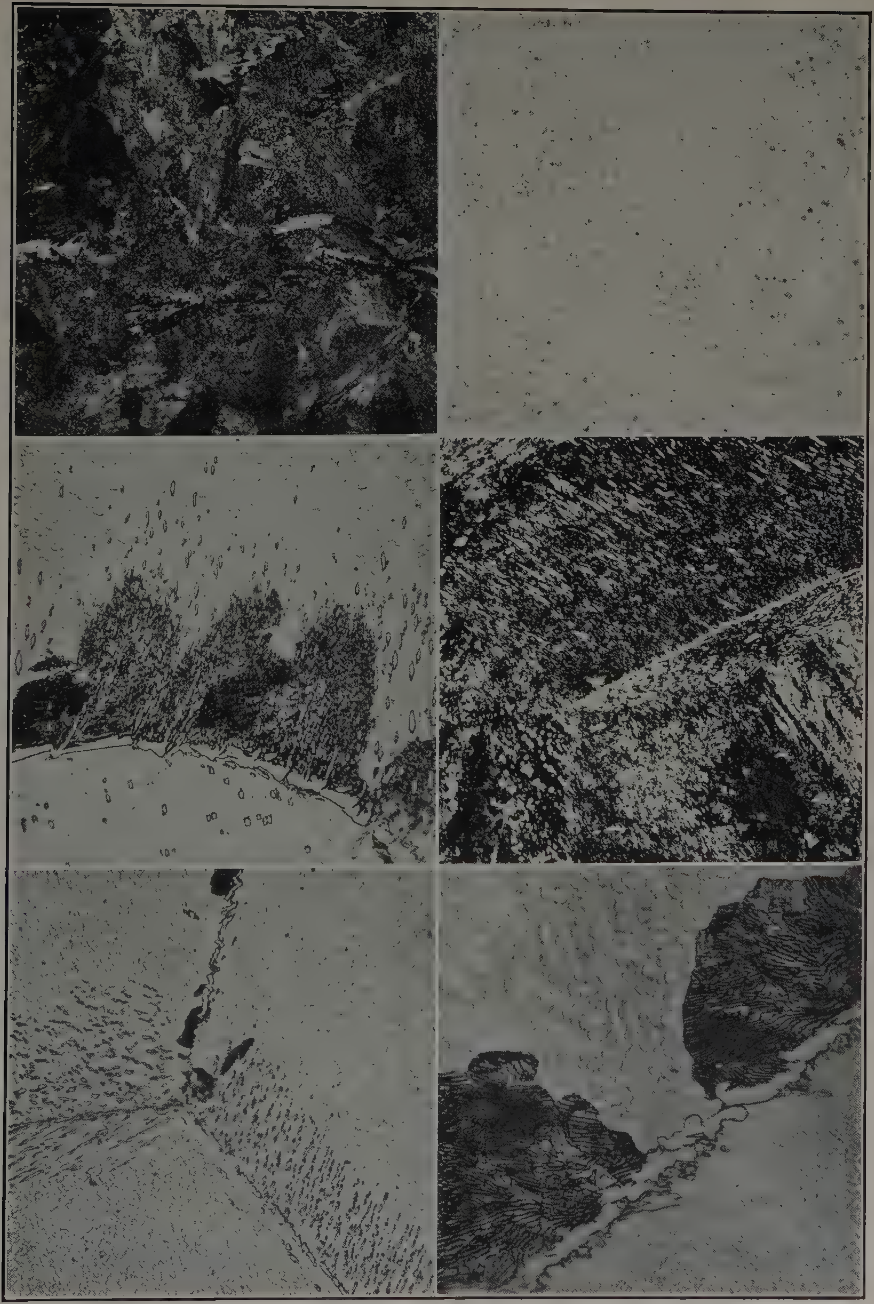
FIGS. 20–25.—ALLOY 577, CONTAINING 11.87 PER CENT ALUMINUM. QUENCHED FROM 900° C. IN SALT BATH AT TEMPERATURE, HELD FOR TIME STATED AND QUENCHED IN ICE WATER. FIGS. 20, 22, 24 AND 25 ETCHED WITH $NH_4 + H_2O_2$, FIG. 21 WITH $HNO_3 + H_2CrO_4$ AND FIG. 23 WITH $FeCl_3 + HCl$.

Fig. 20.—Held at 535° C. 480 sec. × 200.
Fig. 21.—Held at 525° C. 10 sec. × 250.
Fig. 22.—Held at 525° C. 483 sec. × 250.
Fig. 23.—Held at 525° C. 1922 sec. × 200.
Fig. 24.—Held at 500° C. 242 sec. × 250.
Fig. 25.—Same as Fig. 24. × 750.



Figs. 20–25.—Captions on opposite page.

thin films along the old β grain boundaries and after a little longer time developed as thin long plates or needles growing into the body of the grains. The needles changed direction rather frequently and appeared almost curved at a low magnification (Figs. 29 and 30). With increasing time the amount of α rapidly increased, β disappeared after 244 sec. coincident with the appearance of eutectoid, to which the β' gave rise. Eutectoid growth was very slow (see, for example, Fig. 31, after 3844 sec.) and was not complete until 14,940 sec. The final structure showed a considerable proportion of α needles embedded in the fine eutectoid matrix.

Transformation at 450° *C.*—The amount of α found at 450° C. was even greater than that occurring at 475° C. and persisted clearly visible in the fully decomposed alloy. Large amounts of β' were present even in the first alloy and no β remained unconverted to β' after 127 sec. After 240 sec. the well defined structure of α in a homogeneous β' matrix shown in Fig. 32 was formed. Eutectoid was slow in forming and some δ appeared in noneutectoidal form surrounding the α needles (Fig. 33).

Transformation at 425° *C.*—After only 6 sec. at this temperature, the sample consisted almost entirely of β', with a little β and traces of α at the boundaries. Ten seconds left only a trace of β and after 16 sec. the specimen, save for α at the boundary, was homogeneous β' and could not be distinguished from β. α appeared in plate form after 27 sec., the plates being very long and thin. Although α growth was very rapid (see Figs. 34 and 35) the formation of eutectoid was slow and the end of transformation was considerably delayed. The amount of δ in the eutectoid was fairly large, as would be expected on account of the prior impoverishment of β' due to the α growth. In some areas, the δ filled in the space between the α needles and no true eutectoid structure was formed. Figs. 36 and 37 show an intermediate and final sample in the series.

Transformation at 400° *C.*—As in the specimens quenched after 10 sec. at 425° C., it was impossible to identify β' as such in the series, although it is probable that the entire specimen rapidly changed to this phase. Long extraordinarily thin and straight needles or plates[19] of α formed even after

FIGS. 26–31.—ALLOY 577, CONTAINING 11.87 PER CENT ALUMINUM. QUENCHED FROM 900° C. IN SALT BATH AT TEMPERATURE, HELD FOR TIME STATED AND QUENCHED IN ICE WATER. ETCHED WITH $NH_4OH + H_2O_2$ EXCEPT FIG. 27, WHICH WAS ELECTROLYTICALLY ETCHED.

Fig. 26.—Held at 500° C. 1920 sec. × 250.
Fig. 27.—Held at 500° C. 3870 sec. × 200.
Fig. 28.—Held at 475° C. 30 sec. × 250.
Fig. 29.—Held at 475° C. 90 sec. × 250.
Fig. 30.—Held at 475° C. 120 sec. × 250.
Fig. 31.—Held at 475° C. 3844 sec. × 250.

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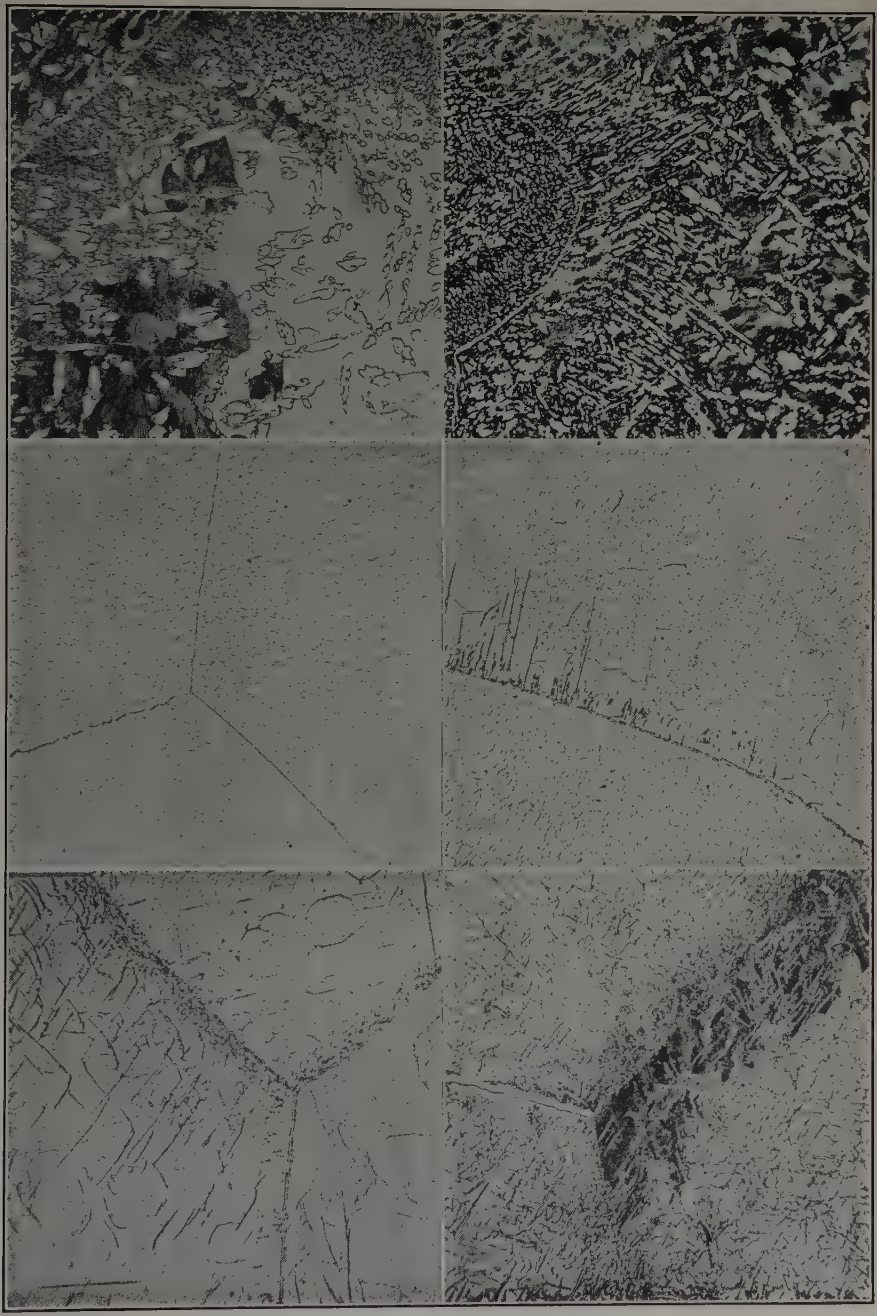
[19] The α is almost certainly in the form of plates, since a thin needle would rarely leave a long trace on the sections but the two-dimensional appearance of the precipitate is that of needles, and that name is customarily applied.



Figs. 26–31.—Captions on opposite page.

33 sec. and these had reached considerable size before the eutectoid commenced to precipitate. Fig. 38 shows a specimen after 1 min. at 400° C., and Fig. 39 after 16½ hr., when the eutectoid is growing. It is interesting to note that as the eutectoid forms from β' in the interstices between the α needles, it also grows appreciably into the latter, leaving these with a very jagged edge or in some cases completely obliterated. This is probably due to the fact that the α is considerably supersaturated with aluminum and δ readily precipitates from it when nuclei are available.

Transformation below 400° *C.*—The course of transformation below 400° C. is very difficult to follow by microscopic examination and it is

TABLE 4.—*X-ray Analysis of Low-temperature* α

Face-centered Cubic Plane Indices	10 Per Cent Aluminum Very Slowly Cooled			11.87 Per Cent Aluminum, Quenched from 900° C. in Salt Bath at 375° C. Held 72 Hr.		
	Spacing, Å	Intensity[a]	A_0	Spacing, Å	Intensity[a]	A_0
				2.250	vw	
111	2.123	s	3.68	2.125	s	3.68
	2.040	m		2.040	m	
				1.953	m	
100	1.832	s	3.66			
110	1.290	s	3.65	1.295	w	3.66
	1.178	vw				
311	1.101	s	3.65	1.110	m	3.68
111(2)	1.051	m	3.64	1.059	vw	3.67
100(2)						
331	0.835	vw	3.64			
210	0.813	vw	3.64			
Average			3.65_2	Average		3.67_4

[a] s = strong; m, medium; w, weak; vw, very weak.

possible that the conclusions which follow are erroneous. Fig. 40 shows a sample quenched from 900° C. in a salt bath at 375° C. and maintained at that temperature for 32 days. At first glance the structure looks like acicular β except for the definiteness of the twin markings. Etching failed to distinguish greatly between these large needles and the undoubted α that was being precipitated in the eutectoid patches at the grain boundaries, and it was concluded that almost the entire specimen had changed

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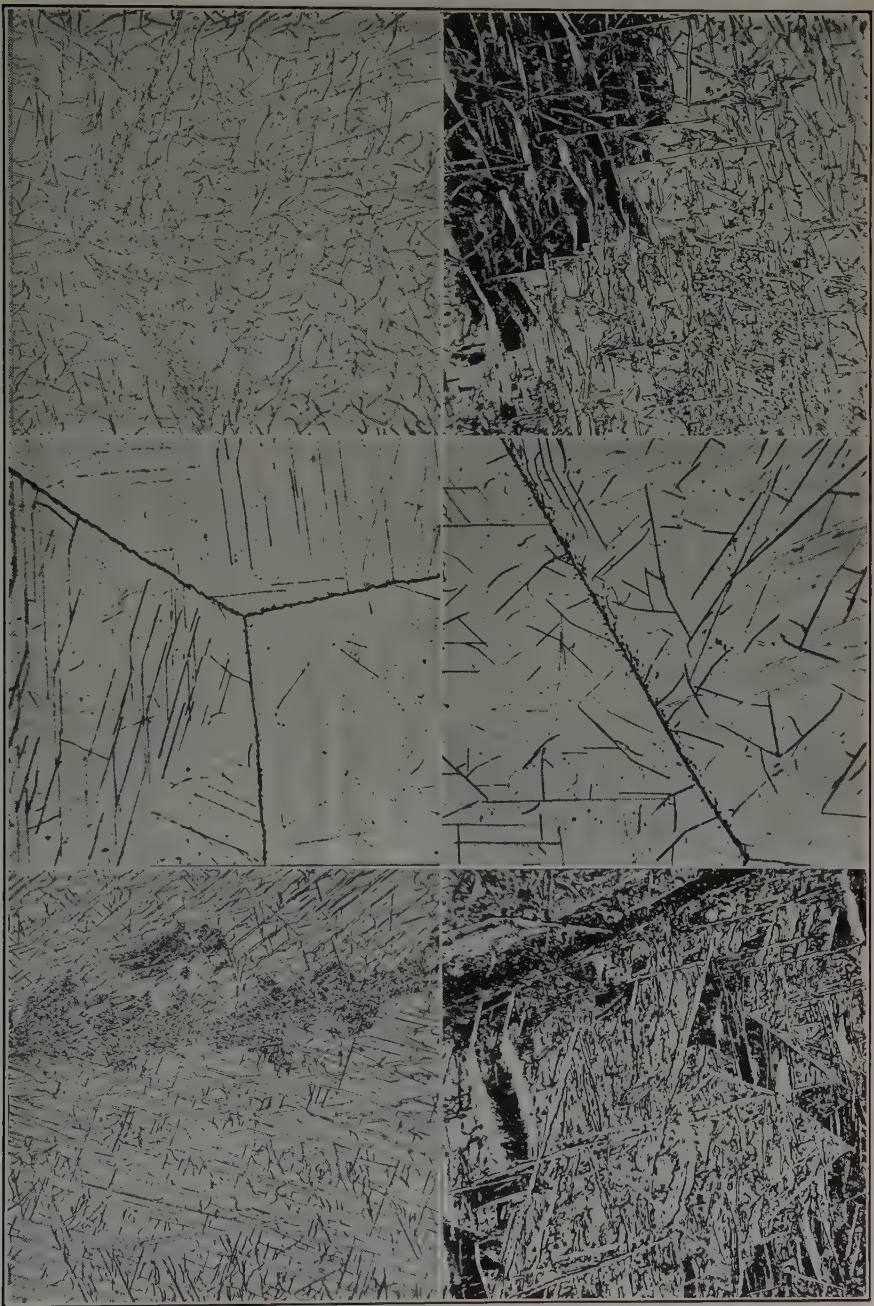
FIGS. 32–37.—ALLOY 577, CONTAINING 11.87 PER CENT ALUMINUM. QUENCHED FROM 900° C. IN SALT BATH AT TEMPERATURE, HELD FOR TIME STATED AND QUENCHED IN ICE WATER. ETCHED WITH $NH_4OH + H_2O_2$.

Fig. 32.—Held at 450° C. 240 sec. × 250.
Fig. 33.—Held at 450° C. 4 hr. × 250.
Fig. 34.—Held at 425° C. 60 sec. × 250.
Fig. 35.—Held at 425° C. 120 sec. × 250.
Fig. 36.—Held at 425° C. 9180 sec. × 250.
Fig. 37.—Held at 425° C. 54 hr. × 250.



FIGS. 32–37.—CAPTIONS ON OPPOSITE PAGE.

to the α constituent, although it was considerably beyond the normal limit of the α phase at this temperature. Specimens from higher temperatures had shown increasing amounts of α coming from β′ and it is not impossible—indeed it is highly probable—that α can have much greater than the customary amount of aluminum in solution when it is in metastable equilibrium with β′.[20]

Apart from the eventual formation of eutectoid after very long periods, there is no definite change in microstructure on heating at 375° C. This can be seen by comparing Fig. 40 with a directly quenched acicular β (Fig. 5), and one is tempted to suggest that acicular β is mainly a highly supersaturated and distorted form of α, much as martensite in steel is based on a highly distorted low-temperature lattice. The analogy between the two structures is close and would bear comparative study. The eutectoid, which finally forms at 375° C., is different in form from its high-temperature prototype and consists of irregular masses of α + δ having no lamellar structure whatever.

FIGS. 38–40.—ALLOY 577 CONTAINING 11.87 PER CENT ALUMINUM. QUENCHED FROM 900° C. IN SALT BATH AT TEMPERATURE, HELD FOR TIME STATED AND QUENCHED IN ICE WATER. FIGS. 38 AND 39 ETCHED WITH $NH_4OH + H_2O_2$, FIG. 40 WITH $K_2Cr_2O_7$.

Fig. 38.—Held at 400° C. 64 sec. × 250.
Fig. 39.—Held at 400° C. 16½ hr. × 500.
Fig. 40.—Held at 375° C. 32 days. × 250.

FIGS. 41–43.—ALLOY 577, CONTAINING 11.87 PER CENT ALUMINUM. ETCHED WITH $NH_4OH + H_2O_2$.

Fig. 41.—Cooled at rate of 192° C. per hour. × 200.
Fig. 42.—Cooled at rate of 126° C. per hour. × 500.
Fig. 43.—Cooled at rate of 25° C. per hour. × 500.

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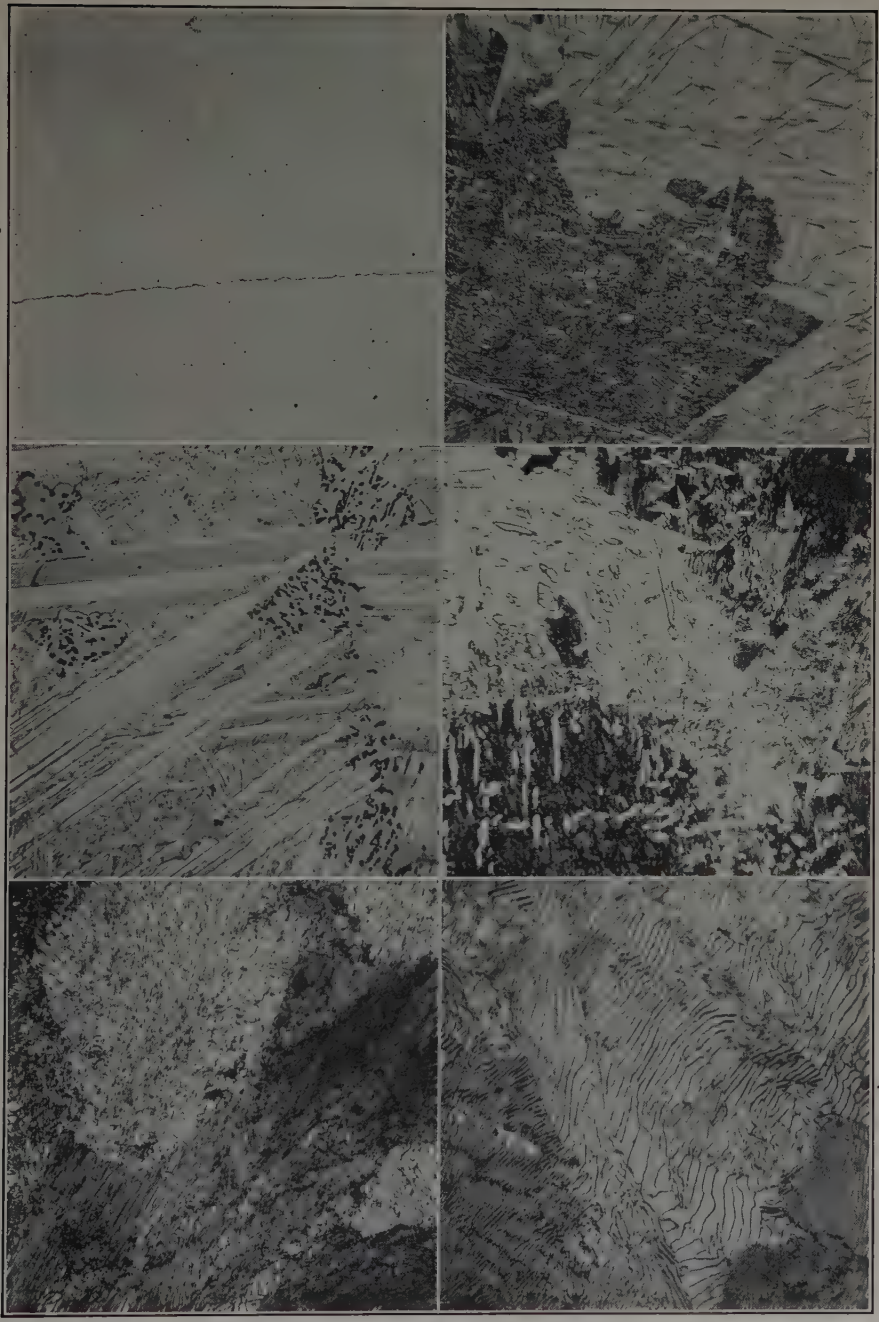
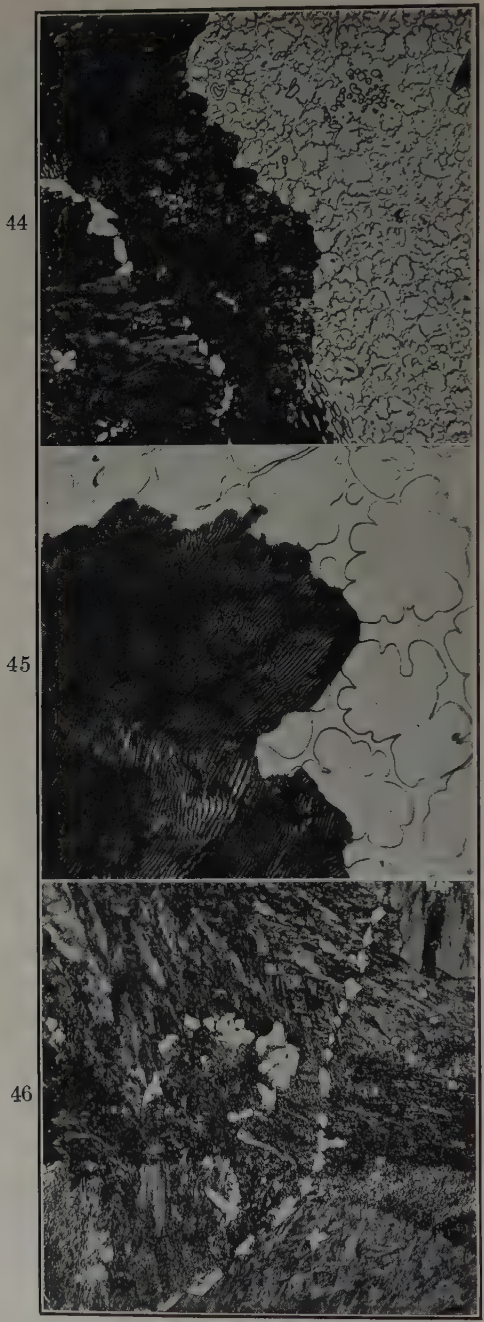
[20] An X-ray diffraction pattern on a General Electric Co. diffraction apparatus was taken of a sample of the eutectoid alloy quenched from 900° C. in a salt bath at 375° C. and held 72 hr. [The authors wish to thank Prof. John T. Norton of the Massachusetts Institute of Technology for making this exposure.] For comparison, an alloy with 10 per cent aluminum annealed at 600° C. and very slowly cooled was run alongside. Table 4 lists the lines obtained. The lines on the diffraction pattern of the alloy quenched to and annealed at 375° C. were, with two exceptions, accounted for by a face-centered cubic lattice of 3.674Å parameter. The 10 per cent aluminum alloy had a parameter of 3.652Å with two lines presumably due to δ, one of which was also present in the eutectoid alloy quenched at 375° C. The remarkable disappearance of the 100 line in the quenched alloy is difficult to account for. Roux and Cournot [*Compt. rend.* (1929) **188**, 172] found a similar occurrence with a 10 per cent aluminum alloy quenched from high temperatures, and found the same additional lines at 1.953 and 2.046Å, which were not present in the slowly cooled alloys. Except for the mysterious disappearance of the 100 line, the sample of eutectoid composition quenched at 375° C. consists principally of alpha, and the increase in parameter shows it to be supersaturated with aluminum—checking our deduction from the microstructure. The β phase, according to the work of Persson [*Ztsch. f. Physik* (1929) **58**, 115] and Obinata (reference of footnote 9), is known to have a body-centered cubic "superlattice" of about 5.835Å parameter, the unit consisting of eight body-centered cubes with a regular arrangement of copper and aluminum atoms.



Figs. 38-43.—Captions on opposite page.



FIGS. 44–46.—ALLOY 577, CONTAINING 11.87 PER CENT ALUMINUM. ETCHED WITH $NH_4OH + H_2O_2$ EXCEPT WHERE OTHERWISE NOTED.

Fig. 44.—Cooled from 600° C. to 500° C. in 45 minutes, quenched. × 200.
Fig. 45.—Same as Fig. 44. Etched with $HNO_3 + H_2CrO_4$. × 1000.
Fig. 46. Quenched from 500° C. after 155 transformations. × 150.

Transformation with Various Cooling Speeds.—Obinata[21] has studied the transformation at comparatively rapid speeds. The transformation during furnace cooling was studied by the authors. Specimens were annealed for 1 hr. at 800° C., furnace-cooled to 600° C., then cooled at constant rates to 350° C. and quenched. The rates of cooling and the structures of the samples were as follows:

Cooling Rate, Deg. C. per Hr.	Structure
About 250	$\beta' + \alpha +$ eutectoid
192	Trace $\beta' + \alpha +$ eutectoid
126	All eutectoid
84	All eutectoid
41	All eutectoid
25	All eutectoid

Typical structures are shown in Figs. 41, 42 and 43. The eutectoid spacing becomes greater as the cooling rate becomes slower, and at the slowest rates there is a tendency for it to be spheroidal. Obviously, the slower the cooling rate, the higher the temperature at which the greater part of the transformation can take place. Some undecomposed β' is seen in Fig. 41.

An excellent example of the mixed β and β' was obtained by cooling in 45 min. from 600° to 500° C. and quenching at 500° C. This sample is shown in Fig. 44 and at a high magnification in Fig. 45. The latter figure shows particularly well the growth of eutectoid indiscriminately through β and β' and the slight difference in color in the eutectoid formed from the two phases.

Effect of Repeated Transformations

The effect of causing the alloy to undergo a number of transformations was investigated, by setting the "on" and "off" contacts of a Leeds & Northrup temperature controller to work over the range 500° to 600° C. Rates of heating and cooling were adjusted so that complete transformation took place in either direction, one complete cycle occupying about 1 hour and 40 minutes.

A sample quenched from 600° C. after 157½ cycles consisted of β and a little proeutectoid δ. Fig. 46 shows a sample quenched from 500° C. after 155 cycles, each cooling from 600° C. occupying 75 min. The photomicrograph shows fine eutectoid and proeutectoid δ, for the aluminum content of the alloy is somewhat in excess of the eutectoid composition.

To ascertain whether the repeated transformation had any effect on the final speed of decomposition, a number of samples that had been given 157 transformations were quenched from 600° C. in a salt bath at 545° C. and single samples were withdrawn and quenched after varying periods of time. A series that had had but one transformation was run at the same time. The following table shows the time of beginning and completion of the transformation. The effect of the repeated transformation was to slow down the completion of the β eutectoid transformation, although the time at which the eutectoid first forms is not affected.[22]

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[21] I. Obinata: Reference of footnote 9.

After	Eutectoid First Forms Between	Transformation Complete
157 transformations	123–252 sec.	1922–3842 sec.
1 transformation	123–240 sec.	975–1921 sec.

It is interesting to note that the amount of δ is rather greater in the samples after many transformations than it was originally. This seems to be due to the fact that the small particles of δ act as nuclei for further precipitation during cooling and for the eutectoid δ to crystallize on. This increases the local concentration of aluminum and the short time allowed above the eutectoid point on reheating was insufficient to eliminate the composition gradient. Further concentration of δ occurs with each transformation until the composition gradient in the β phase becomes so steep that diffusion on heating balances the concentration effect on cooling. Whether this effect is responsible for the delaying of the completion of the transformation is not known.

Electrical Conductivity

The transformation of the copper-aluminum alloy containing 11.87 per cent aluminum was also studied at three temperatures by means of electrical conductivity measurements. The sample used in determining the eutectoid transformation temperature, which had already undergone about six transformations, was employed, the sample being first annealed for ½ hr. at 600° C. then quenched in a salt bath at the desired temperature, its conductivity being determined at frequent intervals until no further change occurred. The conductivity of the salt bath was found to be negligible compared with that of the sample, and it did not introduce complications, although it was in full contact with the specimen and lead wires.

Readings were taken at 555°, 525° and 500° C., which are plotted in Fig. 47. The figure shows that at 555° C., after an initial decrease due to the fall in temperature, the resistance of the sample begins to increase and does so fairly uniformly until it reaches a constant value in about 2 hr. The time is not exactly comparable to that found by microscopic study, although transformation begins at approximately the same moment. It is possible that the electrical conductivity continues to increase after all eutectoid is formed, although since the sample had

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[22] E. C. Bain (Campbell Memorial Lecture, Amer. Soc. Steel Treat., 1932) found grain size to have a great influence on the rate of the austenite-pearlite transformation in steels. It was attempted to explain the change in speed of decomposition after many transformations on this basis, but measurements showed the grain size to be less than that of the main series at 900° C. Specimens consisting of a single crystal, cooled from 900° C., showed first eutectoid appearance in 480 sec., and transformation was complete in 3840 sec., at 545° C. At 475° C. α plates appeared in 125 sec., δ in 1920 sec., and transformation was complete after 7800 sec.—less than the time required for the fine-grained material. Within the range studied, the effect of grain size is therefore not great, but even the polycrystalline samples were of such large size (about 0.8 mm. average grain diameter—far larger than the largest size studied by Bain) that the effect of the grain boundary was minimized and the transformation depended mainly on intracrystalline nuclei.

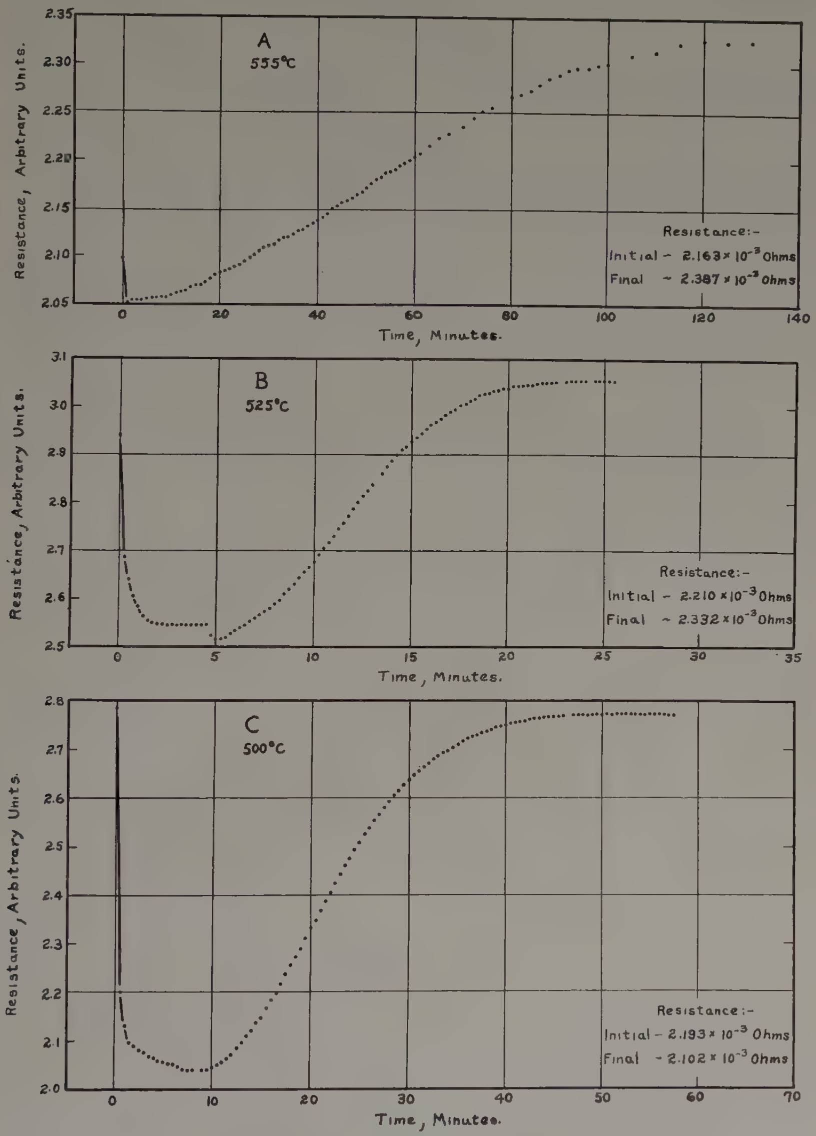

FIG. 47.—TRAVSFORMATION OF EUTECTOID AT VARIOUS TEMPERATURES AS SHOWN BY ELECTRICAL RESISTANCE CURVES.

previously undergone several transformations, the difference may have been due to this. At 525° C., the resistance drops rapidly when first quenched, remains constant between 2.5 and 4 min., then drops suddenly, after which it increases uniformly to a constant value after about 23 min. The second slight drop in the curve is undoubtedly caused by the precipitation of α, which makes its appearance rather rapidly. As eutectoid is formed, the increase in resistance occurs. The time at which α precipitates, as indicated by the rapid drop in resistance agrees with that found by microexamination, as also does the first appearance of eutectoid. The conductivity curve indicates the transformation to be complete in about 23 min. while microscopic examination on separate samples showed it to be complete in 16 min. At 500° C., the drop in resistance is rapid when first quenched, followed by a gradual decrease to a minimum after about 9 min., this gradual decrease being caused by precipitation of α. A uniform increase in resistance then occurs till it becomes constant after 50 minutes.

The conductivity curves give a general idea of the progress of the transformation rather than an exact indication of the time at which the several phases in question appear or disappear. For example, at 500° C. the first appearance of δ in the eutectoid may be masked by the precipitation of large amounts of α, so that it is impossible to tell at just what time δ first appears.

Hardness of Transformed Samples

Rockwell hardness measurements were taken on all of the samples in the transformation series at various temperatures. These are given in the table of microstructures (Table 2) and selected values are plotted in Figs. 48 and 49.

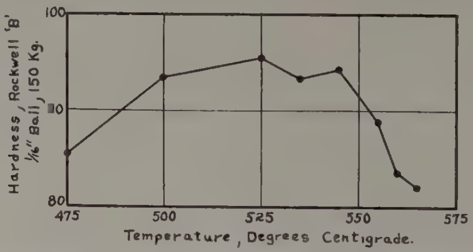

FIG. 48.—HARDNESS OF EUTECTOID FORMED AT VARIOUS TEMPERATURES.

The final hardness of the specimens consisting entirely of eutectoid increases as the temperature of formation is lowered from 565° C. to a maximum at 525° C., followed by a decrease at lower temperatures, as is shown in Fig. 48. The increase with lowered temperature is due to decreasing plate size of the eutectoid, while the drop in hardness below 525° C. is caused by the α phase, which appears prior to the eutectoid and which remains distributed throughout it when the transformation is complete. After the eutectoid had been formed at any temperature, further annealing was found to have no effect on its hardness. At temperatures of 565° to 535° C. there is first a slight decrease in hardness, after which the formation of eutectoid causes a marked increase in hardness.

Fig. 49 shows the variations of hardness with time at several temperatures. Comparing the hardness with the microstructures, there is no noticeable difference between the hardness of β and β' which suggests that Obinata's homogeneous β' obtained by cooling was in reality a fine $\alpha + \delta$ complex. At 525° and 500° C., the precipitation of α causes a slight decrease in hardness, which is followed by a marked increase as time proceeds and eutectoid is formed.

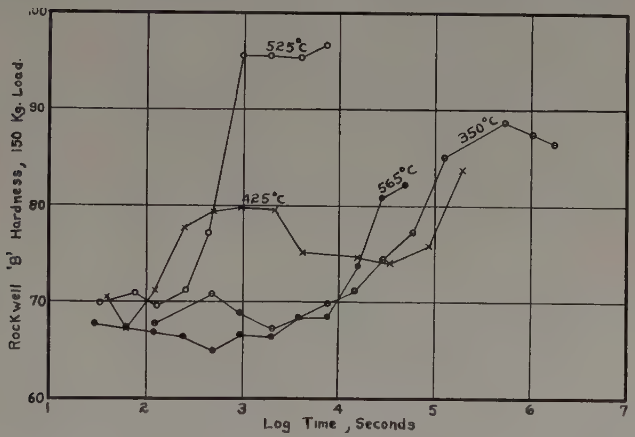

FIG. 49.—TRANSFORMATION HARDNESS CURVE AT VARIOUS TEMPERATURES.

In the range 475° to 400° C., the first precipitation of α increases the hardness, probably owing to critical dispersion, followed by a decrease as more is formed, and a final increase as δ is precipitated. The low-temperature α formed at 375° C. and below has a much greater hardness than β; again showing its similarity to martensite.

There was no appreciable change in hardness of quenched β on standing at room temperature for a period of 4½ months.

Transformation on Reheating after Quenching

Samples quenched from a temperature above 570° C. to room temperature, and annealed at temperatures below the transformation point, do not show the regular lamellar or spheroidal eutectoid structure. After this treatment the structures are more or less Widmanstätten in form, depending on the reannealing temperature and the rate at which the sample is heated. This has been shown by earlier investigations.

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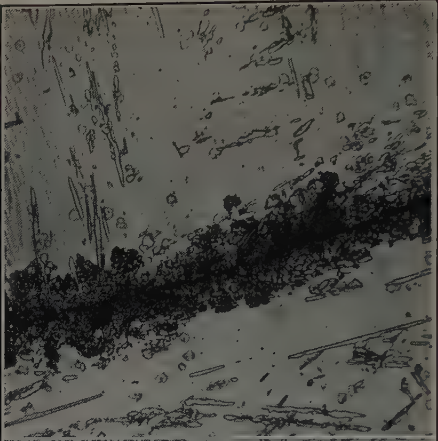

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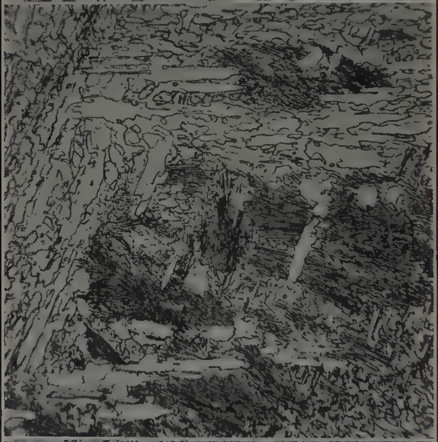

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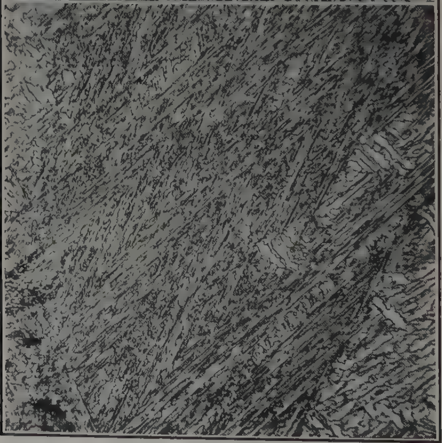


Figs. 50–52.—Alloy 577, containing 11.87 per cent aluminum. Quenched in water from 900° C. and given the treatments described. Etched with $NH_4OH + H_2O_2$.

Fig. 50.—Annealed 122 sec. in salt bath at 550° C. Quenched. × 250.
Fig. 51.—Annealed 19 hr. in salt bath at 550° C. Quenched. × 250.
Fig. 52.—Heated to 550° C. in 1 hr. 20 min., held 17½ hr. Quenched. × 250.

At 550° C., instead of the slow formation of eutectoid which occurs on direct cooling to this temperature, fine long needles of α make their appearance in a very short time (less than 30 sec.). A few almost hexagonal crystals of δ appear, having no direct connection with the α and definitely not eutectoidal in form (Fig. 50). As time increases, β rapidly decomposes, giving rise to a small quantity of eutectoid at the grain boundaries, but mainly to wide needles of α and massive δ filling in the spaces between these (Fig. 51). It requires 16 min. to complete the transformation at this temperature. If the specimen is heated slowly to 550° C. eutectoid is entirely absent and the structure consists of groups of α plates (Fig. 52). The rather remarkable growth of independent α and δ is due probably to the formation of nuclei at low temperatures, either during the original quenching or during reheating. As the direct transformation series showed, needles or plates form very quickly below 400° C. The formation of noneutectoidal δ is less easy to account for than α, but since α is removed from β the latter must become supersaturated and δ may then separate at higher temperatures as a proeutectoid constituent.

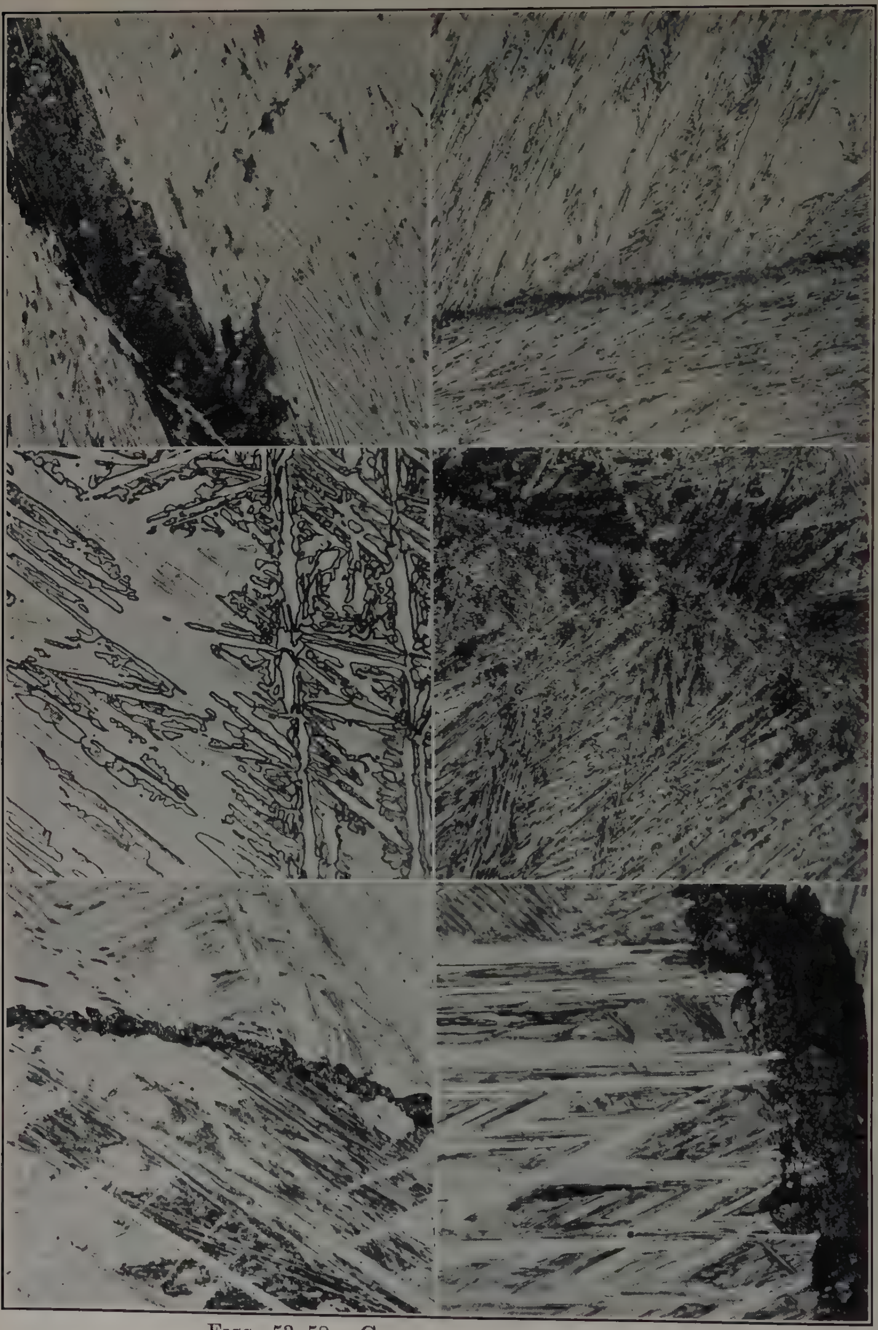
When the quenched samples are quickly reheated to 500° C., the amount of eutectoid is somewhat greater than at 550° C., but the predominating element in the structure is again the α, which extends as long parallel needles separated by β or more probably β', which gives rise to more α and massive δ as it decomposes. About 25 per cent of β' decomposes to a normal eutectoid structure. Complete transformation occurred after 30 min. Figs. 53 to 56 are typical of this series, Fig. 53 showing the formation of α and δ both eutectoidal and noneutectoidal in form. Fig. 55 shows at high magnification the growth of α needles and δ filling. At 500° C. heating slowly does not affect the structure greatly, neither does previous annealing at a lower temperature prior to heating to 500° C.

Although the β is heavily striated and eutectoid commences to form soon (Figs. 57 and 58) there is no visible precipitation of α on reheating rapidly at 450° C. until after 1800 sec. It is highly probable, however, that α in submicroscopic form is separated in numerous heavy striations in the β, for the needles when they are identifiable follow the same directions, although they are much coarser. A typical partly decomposed sample is shown in Fig. 59. Transformation is complete in 4 hr., a large part of the structure being eutectoidal. Slow heating to temperature is without effect.

The decomposition on reheating to temperatures below 450° C. following quenching was not studied. It is believed that the structure observed would not be greatly different from those resulting from direct transformation at these temperatures.

Effect of Tin on Transformation

In the aluminum-tin-copper system there is known to be a phase similar to β' but stable at room temperatures. Suspecting that this was



FIGS. 53–58.—CAPTIONS ON OPPOSITE PAGE.

identical with β' but rendered stable by the addition of tin, two alloys were made up and the transformation studied by the methods applied to the copper-aluminum eutectoid. The microstructure observed after various times is shown in Table 5.

TABLE 5.—*Transformation of Copper-aluminum-tin Alloys*

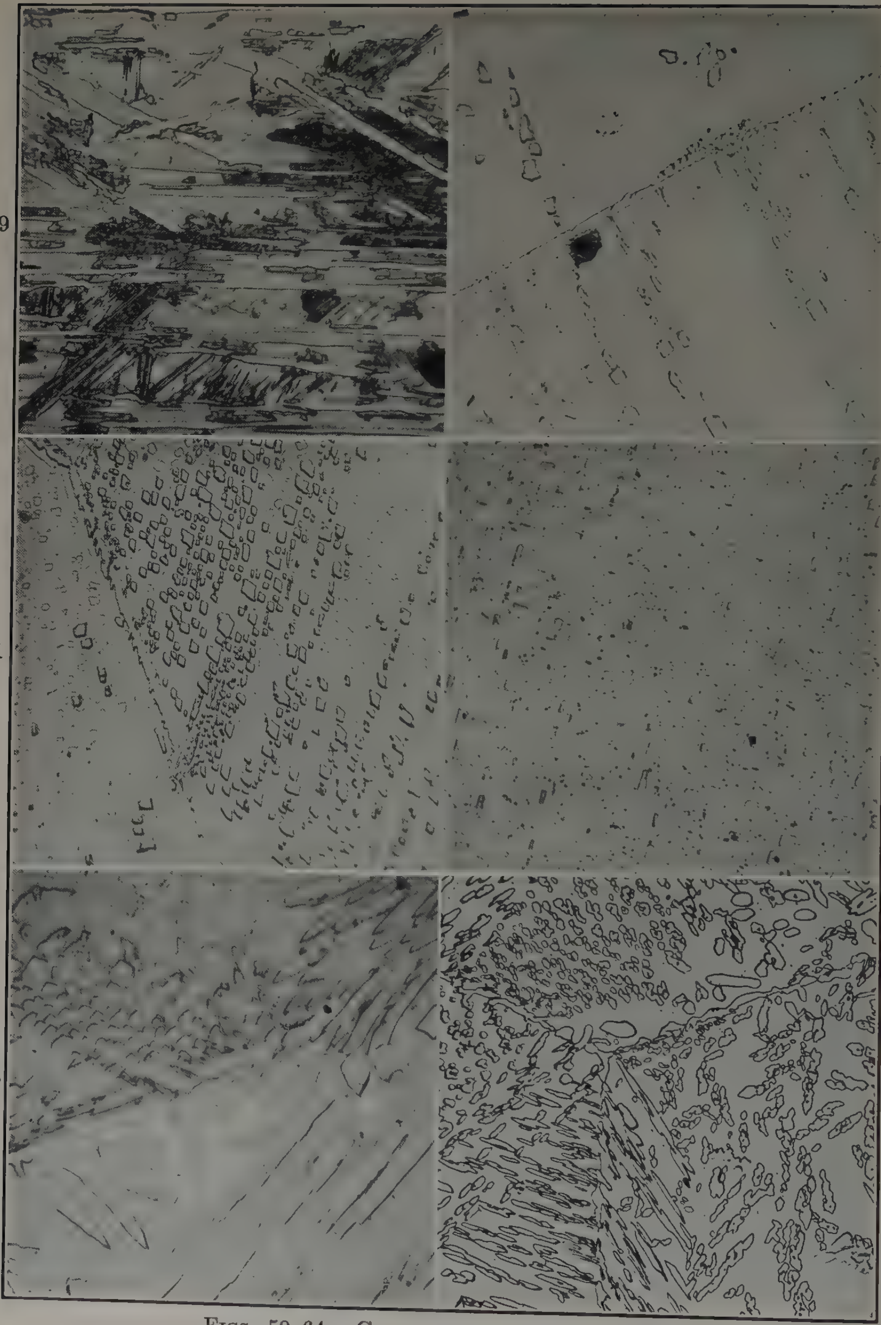
Annealed 1 hr. at 900° C. and Quenched in Salt Bath Maintained at 535° C.

Alloy	Time in Bath, Sec.	Structure
Alloy 727. Cu, 87.7 per cent; Al, 11.3; Sn, 1.0	30	β
	61	β
	121	$\beta + \beta' + \alpha$
	240	$\beta + \beta' + \alpha$
	481	$\beta + \beta' + \alpha + E$
	963	$\beta + \beta' + \alpha + E$
	1923	$\beta + \beta' + \alpha + E$
	3843	$\alpha + E$
Alloy 729. Cu, 87.2 per cent; Al, 10.8; Sn, 2.0	31	β
	60	$\beta + \alpha$?
	120	$\beta + \alpha$?
	243	$\beta + \beta' + \alpha$
	483	$\beta + \beta' + \alpha$
	961	$\beta + \beta' + \alpha$
	1920	$\beta + \beta' + \alpha$
	3843	$\beta + \beta' + \alpha + E$

Both alloys quenched in water from 900° C. showed acicular structures. Fig. 60 shows a stage in the transformation of the 1 per cent alloy. Here β' is shown forming particularly at the grain boundary, with α precipitation in it. The peppered appearance is due either to β' or α nuclei forming in the main mass of β. Fig. 61 shows progress in the transformation at a grain boundary in the 2 per cent alloy. More β' is present here and α is precipitating in it. Fig. 62 shows β' regularly orientated in the center of a grain in the same sample. Fig. 63 shows a still later stage with β' changing over massively to δ. Fig. 64 shows α + stable β' in an alloy containing 10 per cent aluminum, 4 per cent tin, slowly cooled from 900° to 525° C., held 24 hr. at 525° C. and quenched. Although large amounts of tin stabilize β', small amounts do not hasten, indeed seem rather to delay, the formation of transitional β' on cooling.

FIGS. 53–58.—ALLOY 577, CONTAINING 11.87 PER CENT ALUMINUM. QUENCHED FROM 900° C. IN WATER. REANNEALED IN SALT BATH AT TEMPERATURE FOR TIME NOTED AND QUENCHED. ETCHED WITH $NH_4OH + H_2O_2$.

Fig. 53.—Reannealed at 500° C. 450 sec. × 250.
Fig. 54.—Reannealed at 500° C. 900 sec. × 250.
Fig. 55.—Same as Fig. 54 × 1000.
Fig. 56.—Reannealed at 500° C. 4 hr. × 250.
Fig. 57.—Reannealed at 450° C. 450 sec. × 250.
Fig. 58.—Reannealed at 450° C. 903 sec. × 500.



FIGS. 59–64.—CAPTIONS ON OPPOSITE PAGE.

Etching

As an etching reagent for microscopic examination of the alloys a 50 per cent 0.90 sp. gr. ammonium hydroxide solution with additions of 10 per cent of 9 per cent hydrogen peroxide was mainly used. At first, this was the only reagent found that would clearly distinguish the β' phase from the β; in fact, with other etching solutions, such as potassium bichromate, ferric chloride and ammonium persulfate, the presence of the former phase is entirely concealed.

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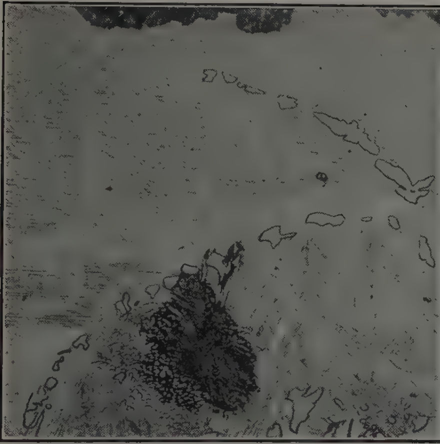
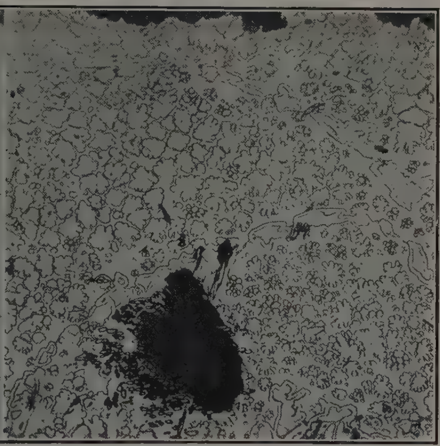
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FIG. 65.—SAME AS FIG. 44. ETCHED WITH $K_2Cr_2O_7$. × 200.
FIG. 66.—SAME SPECIMEN AND FIELD AS FIG. 65. ETCHED WITH $NH_4OH + H_2O_2$. × 200.

Fig. 65 shows the same sample as that shown in Fig. 44, etched with potassium bichromate and sulfuric acid, an etching reagent which works perfectly with almost all copper alloys. On this specimen it shows eutectoid, proeutectoid δ and α in a ground of well defined acicular β. The same field given a deep etch with ammonia and peroxide solution is shown in Fig. 66, in which the most conspicuous constituent is the β'. Although photographically it is difficult to distinguish between α and δ

FIGS. 59–64.—TRANSFORMATION OF VARIOUS ALLOYS. ETCHED WITH $NH_4OH + H_2O_2$.

Fig. 59.—Alloy 577, containing 11.87 per cent aluminum. Quenched from 900° C. in water. Reannealed in salt bath at 450° C. for 2 hr. and quenched. × 500.

Fig. 60.—Alloy 727, containing 11.3 per cent aluminum, 1.0 per cent tin. Quenched from 900° C. in salt bath at 535° C. Held for 481 sec. and quenched. × 250.

Fig. 61.—Alloy 729, containing 10.8 per cent aluminum, 2.0 per cent tin. Quenched from 900° C. in salt bath at 535° C. Held for 961 sec. and quenched. × 250.

Fig. 62.—Same as Fig. 61. × 500.

Fig. 63.—Alloy 729, containing 10.8 per cent aluminum, 2.0 per cent tin. Quenched from 900° C. in salt bath at 535° C. Held for 3843 sec. and quenched. × 500.

Fig. 64.—Alloy 708, containing 10.0 per cent aluminum, 4.0 per cent tin. Annealed 24 hr. at 525° C. and quenched. × 200.

visually the difference in color is evident and permits definite identification. Occasionally, as for example in Fig. 63, a blue color filter was used to show δ as white, but most photographs were taken using a green (Wratten B) filter and the constituents merely outlined.

After most of the photographs in this paper were taken, a new and better reagent was discovered. This consisted of dilute nitric and chromic acids, the optimum composition of the mixture having not yet been determined. The following was satisfactory: HNO_3 (1.42 sp. gr.), 40 grams; CrO_3, 25 grams; H_2O, 35 grams. This was used for Figs. 45 and 21, which show how clearly it defines β' and β.

Theory of Formation of β'

Although the electrical conductivity curves obtained by all workers except Obinata do not show anything to indicate that the eutectoid transformation under equilibrium conditions is other than a simple change from β to $\alpha + \delta$, Obinata's work showing a double transformation cannot be neglected. Probably the discrepancy was due to the presence or absence of impurities modifying the change. Matsuda's evidence for the presence of β' was the high electrical conductivity and small dilatation of alloys rapidly cooled, which Obinata regarded merely as confirmatory evidence. The microscopic evidence given in the present paper suggests that the low electrical conductivity and high density is due to supersaturated α, which, as we have shown, occurs in large quantities during cooling and which would have a predominating effect on the conductivity even if β' were previously or simultaneously formed.

From analogy with the copper-tin and copper-zinc diagrams one would expect complicated reactions, and in the ternary system copper-aluminum-tin Stockdale[23] and others have definitely established the presence of a phase microscopically indistinguishable from β but which does not decompose in cooling. Just as in the copper-zinc diagram it seems that the β almost forms a eutectoid and actually does so when small additions of other elements, for example tin, are made, the copper-aluminum system can be regarded as almost *not* forming a eutectoid and tending to form a second phase similar to β but of higher stability at lower temperatures. The mechanism of the formation of α and β' can be accounted for in this way.

It is theoretically possible to assume for any composition any space lattice arrangement we like and to compute the potential energy of the arrangement. Only that phase of lowest potential energy is capable of actual existence, however, since the others are unstable. There may easily be two possible structures of almost equal stability for the same composition, but however nearly it approaches the phase of lower energy the phase of higher energy cannot have any real existence. If the energy of the second phase decreases at a more rapid rate at lower temperatures than the first, there will be an intersection of the curves, at a point below which the second phase will be more stable. Occasionally, both the phases will be less stable at a still lower temperature than some other arrangement, and this double decomposition is probably what exists in the copper-tin diagram where the β and γ phase are very similar in nature and decompose eutectoidally at temperatures close to each other. If the phase that is least stable decomposes at a higher temperature than the other it will never make its appearance. On the other hand, it is not impossible that, although in equilibrium conditions the β phase is the more stable, below the point at which β decomposes to $\alpha + \gamma$ the β and β' curves intersect, rendering β' the more stable of the two phases. This is shown

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[23] D. Stockdale: *Jnl.* Inst. Metals (1926) **35**, 181.

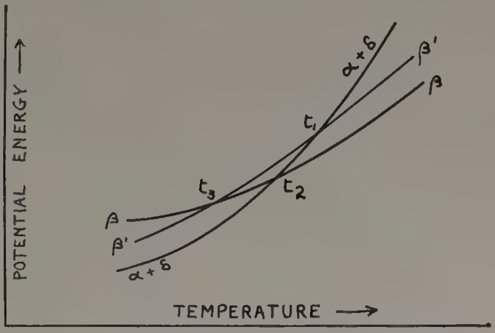

FIG. 67.—HYPOTHETICAL POTENTIAL ENERGY CURVES.

diagrammatically in Fig. 67, where three hypothetical potential energy curves for the eutectoid composition are plotted. The point t_2 corresponds to the eutectoid temperature, for it marks the point where β corresponds to less energy than $\alpha + \delta$. The curve for β' is always above the minimum but intersects the $\alpha + \delta$ curve at t_1, forming the hypothetical eutectoid $\beta' \rightleftharpoons \alpha + \delta$, and the β curve at t_3, the transformation point $\beta \rightarrow \beta'$. On cooling below t_2 but above t_3 β will decompose directly to $\alpha + \delta$. If it is retained by cooling at a sufficiently rapid rate to below t_3, it will be able to change to β', which is at that temperature more stable than β but less stable than $\alpha + \delta$. In view of the evident similarity of structure between β' and β this transformation takes place easily, and so the phase β' has an independent though transitional existence. β can, of course, decompose directly to $\alpha + \delta$ without β' being involved, and the final result is a balance between the rate of transformation to β' and the range of decomposition of both β' and β to $\alpha + \delta$.

This theory does not take into account the formation of α. The phase β' is, judging from its etching characteristics, somewhat similar to β

but of higher aluminum content. An alloy consisting of pure β of equilibrium eutectoid composition is therefore in the metastable $\alpha + \beta'$ region, and α will separate out. In view of the fact that α in pseudoequilibrium with β' undoubtedly contains more aluminum than equilibrium α it would be possible to obtain almost all the alloy in the α form. Jette, Westgren and Phragmén[24] found a quenched sample of eutectoid composition to contain far more α than the slowly cooled alloy, and our own microscopic examination and X-ray patterns have shown that samples quenched to temperatures in the neighborhood of 400° C. and allowed to transform there consist almost entirely of α.

Fig. 68 is an attempt to show the possibility of α formation. The heavy lines represent the true equilibrium diagram. The heavy dashed lines are merely the continuation of the $\alpha/\alpha + \beta$ boundary and show clearly that an alloy of true eutectoid composition, if supercooled even without decomposition of β, would be supersaturated in relation to α. The light lines show the hypothetical β' phase, t_1 representing its eutectoid temperature. The $\alpha/\alpha + \beta'$ line would be expected to be at a higher aluminum content than the equilibrium line because β' contains more aluminum and is less stable. This line continued to lower temperatures will intersect the line t_3, which represents the transformation from β to β', and thereafter is a true metastable line, although above t_3 β' cannot possibly exist. The α boundary is displaced considerably from the equilibrium limit, and is shown as extending actually beyond the equilibrium eutectoid composition. This diagram is entirely hypothetical, for we have no means of determining the shift of the composition of α in equilibrium with β', but there is little doubt that some such mechanism actually occurs.

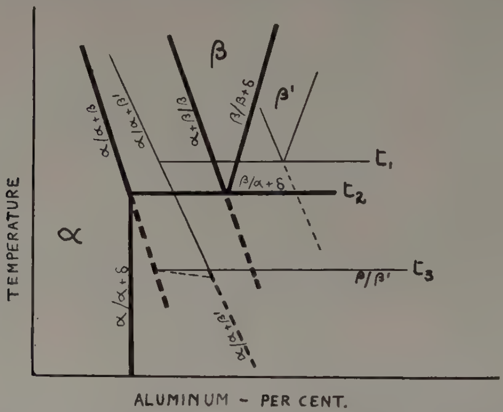

FIG. 68.—HYPOTHETICAL DIAGRAM SHOWING POSSIBILITY OF OBTAINING SUPERSATURATED α OF EUTECTOIDAL COMPOSITION.

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[24] E. R. Jette, A. F. Westgren and G. Phragmén: *Jnl.* Inst. Metals (1924) **34,** 193.

An alternative theory for the formation of β' could be based on a submerged transformation being affected less than the normal eutectoid by an increased rate of cooling. There would then be a critical rate beyond which the submerged transformation would occur.

SUMMARY

The decomposition of an aluminum-copper alloy containing 11.87 per cent aluminum was studied microscopically by cooling samples directly from the β field in a salt bath maintained at constant temperatures below the eutectoid point (which has been redetermined as 570° ± 1° C.) and quenching after various periods of time. Immediately below the eutectoid temperature the rate of formation of eutectoid was very small and at 565° C. transformation did not commence for 1 hr. and was not complete until after 10 hr. At 535° C. the rate of transformation was greatest and complete transformation occurred in 7 min. Lower temperatures increased the time for complete transformation, up to about 5 days at 400° C., below which the microstructures were difficult to interpret. The temperature of 535° C. also marked the appearance of a transitional phase not represented on the equilibrium diagram, and from this phase, called β', α needles or plates grew with extreme rapidity. This transitional β' phase is a new observation and is not identical with the transitional phase indicated by the electrical conductivity curves of Obinata and Matsuda, whose results were probably due to alpha precipitation. The phase is difficult to show microscopically and is not shown by the etching reagents usually used for aluminum-copper alloys. The amount of α was greater the lower the temperature, and it is believed that below 400° C. almost the entire specimen became α, although the equilibrium limit of solubility of aluminum in the α solid solution is only 9.8 per cent. A theory is advanced to account for the transitional phase and for the formation of supersaturated α. The change of microstructure occurring during reheating quenched samples was also studied. These conclusions were arrived at entirely by means of a microscopic study, but corroborative data were obtained from X-ray diffraction studies, hardness measurements and electrical conductivity determinations.

ACKNOWLEDGMENTS

Mr. W. H. Bassett, Metallurgical Manager of The American Brass Co., has had general supervision of the work described herein. For this and for the inspiration of contact with him, the authors express their thanks.

DISCUSSION*

(Robert F. Mehl presiding)

C. H. Mathewson, New Haven, Conn. (written discussion).—The authors have given a complete record of the change in microstructure at every stage of the transformation from β to eutectoid in the copper-aluminum system. This work taken in connection with the X-ray investigation of quenched β by Ageew and Kurdjumow leads to some confusion concerning the meaning of the term β′ used by both authors. Smith and Lindlief describe as acicular β the structure element to which Ageew and Kurdjumow, using the term β′, have ascribed a deformed cubic lattice with one set of planes of form {111} having a spacing somewhat different from that of the others. From Smith and Lindlief's experiments, it is apparent that acicular β is formed by ordinary quenching at any temperature above the eutectoid point, or in transitory form by quenching (from 900° C.) into a salt bath held at any temperature below the eutectoid point. The microstructurally unique β′ of Smith and Lindlief, formed under certain specified conditions of quenching temperature and rate, is therefore a newcomer in the system and we must now distinguish between the original β, stable above the eutectoid temperature, quenched acicular β (or the first β′), and this new "β′" occurring in the form of "rosette-shaped particles."

All authors agree that acicular β is in a strained condition and it is therefore possible that the change from this to Smith and Lindlief's β′, which occurs as an early stage in a relatively rapid series of transformations pointed towards the normal eutectoid structure, is in the nature of a granulation (recrystallization) process without change of crystal structure.

Concerning the mechanism of formation of β′ (acicular β), Ageew and Kurdjumow propose a rapid metastable rearrangement of the β lattice when the normal development of α and δ at the eutectoid point is prevented by quick cooling and the consequent failure of the prerequisite adjustment of concentration by diffusion to occur. This rearrangement of β is likened to the change that occurs in the process of mechanical twinning and, although no detailed discussion of this is given in the paper, continued reference is made to points of similarity between this transformation and that of austenite to martensite as described in a recent paper by Kurdjumow and Sachs;[25] and therein attributed to a shearing process of this character which is analyzed in considerable detail.

The present transformation would appear to require a shearing movement on each plane of a given {110} family in the body-centered β lattice of one-sixth of an atom to atom distance in the direction of form [110].[26] This would give the general arrangement of the face-centered cubic lattice with a distorted {111} plane occupying the position of the shear plane from the other lattice. Moreover, the distance between the planes of this family in the new lattice would also constitute a distortion as it would be the (unrelated) distance between planes of a family {110} in the other lattice. The distorted (unequilateral) triangular arrangement of atoms on the above set of planes of form {111} could now be removed by another shear of just the right amount along planes of a family {211} normal to {111}, thus perfecting a structure in which three families of {111} planes would have the same spacing. The shearing operations may be followed by reference to Kurdjumow and Sach's Figs. 31 to 34.

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* Many of the following discussions refer to a paper by N. Ageew and G. Kurdjumow, which was presented from manuscript at the A.I.M.E. meeting in February, 1933, under the title of The Metastable Solid Solution β′ of the Copper-aluminum Alloys. A brief preliminary note by these authors was published in *Physikal. Ztsch. d. Sovjetunion* (1932) **2,** 146.

[25] G. Kurdjumow and G. Sachs: Über den Mechanismus der Stahlhärtung. *Ztsch. f. Physik* (1930) **64,** 325.

[26] Only one such direction occurs in a given plane of form {110}.

A structure of this general nature, intermediate between those of the body-centered and face-centered cubic lattices, seems to have been found by Ageew and Kurdjumow. A further small adjustment of dimensions would give the α phase in normal form. The formation of the δ phase must be left for future consideration along with the more precise determination of the β' structure and correlation of these crystallographic features with the geometry of the acicular markings in quenched β.

Even the present semiquantitative deductions should offer a measure of satisfaction to Smith and Lindlief, who write on page 88 of their paper, "one is tempted to suggest that acicular β is mainly a highly distorted form of α, much as martensite in steel is based on a highly distorted low-temperature lattice. The analogy between the two structures is close and would bear comparative study."

The twin markings to which they refer (p. 86) should now be regarded as markings produced by a shearing process not unlike that of twinning but carried just far enough to produce, not twinning, or definite reorientation of the pre-existing structure, but a changed lattice. To thus initiate the change from one lattice to the other requires only half the shearing movement necessary for twinning in the face-centered cubic lattice.

It would seem that in this case the structural change should be rendered apparent by the presence of the plane of shear as a composition plane between original and transformed β just as twinning is made evident by the presence of similar (twinning) planes that give rise to the familiar straight line boundaries in the microstructure.

This theory of formation of the acicular structure might be tested by attempting to locate the hypothetical composition planes in relation to both the original and the transformed lattice, utilizing the methods commonly used in studying segregate structures.

R. F. MEHL, Pittsburgh, Pa. (written discussion).—The photomicrographs prepared by Dr. Smith and Mr. Lindlief are very good in view of the difficulties offered by these alloys, and I do not remember seeing a more complete study of any one alloy composition; such a complete study is amply justified by the complexities attending alloy transformations, complexities which have become apparent in nonferrous alloys only within the last few years.

Many of the structures shown bear striking resemblance to those shown in the decomposition of β brass by Dr. Marzke and myself two years ago, and further illustrate the analogies in microstructure of decomposition products in structurally analogous systems. Fig. 61, showing the formation of the α phase, is very much like Figs. 4, 5 and 6 presented by Mr. Marzke.[27] I am inclined to believe that the apparently curved α plates in Figs. 30, 32 and 35 represent branches of straight plates, reasoning by analogy from similar structures observed by Marzke and by Weerts in Germany, and, accordingly, that these particles of α are not needles but plates, since it has been shown that α forming from β in the copper-zinc system at low temperatures takes the form of true plates, though at high temperatures it takes the outward form of true needles.

Acicular β is a structure of peculiar interest, because of its analogy with martensite. In many ways it looks like martensite, but in contrast to martensite appears to contain large twins. Martensite, formed by the precipitation of body-centered cubic α iron from face-centered cubic austenite, shows a maximum of four traces on the surface of polish, corresponding to precipitation on octahedral planes. Acicular β

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[27] A. I. M. E. Contribution 29. (See page 64.)

probably represents the formation of face-centered cubic α from body-centered cubic β; crystallographically it is the reverse case of the formation of martensite. By analogy with the crystallographic mechanism for such transformations in other systems demonstrated by Smith and by Marzke in this country and by Weerts in Germany, we may expect the acicular markings to represent traces of the dodecahedral planes, showing a maximum of six. May I ask whether the authors have prepared frequency curves for this structure? In studying the structure these would be interesting and valuable.

The new β′ phase which the authors have discovered is puzzling. In some of the photomicrographs it resembles the γ phase formed in the slow cooling of hypereutectoid copper-zinc alloys. Doubtless it bears a relationship in orientation to the parent β phase, for the outlines of the separate β′ areas are frequently symmetrical, and also because on further transformation it gives rise to oriented α needles and plates.

I am inclined to agree with the authors that the constituents in the pearlitic eutectoid are oriented with respect to the matrix phase. The observation that slip planes run parallel through much of a single pearlitic area is rather suggestive of this; years ago Rosenhain observed a similar behavior in eutectics. Indeed, it now seems likely that all transformations in the solid state lead to oriented structures. This has been demonstrated for Widmanstätten structures and for several recrystallization structures. An experimental demonstration upon eutectoids, however, is attended by many difficulties.

The observation on direction of growth of the pearlitic structure is important, I think. Similar observations were made by Bain for pearlite in steels. It seems to me that these observations will require a modification of the usual reciprocal supersaturation theory of eutectoids, for it seems fairly obvious that the two constituents deposit essentially simultaneously.

The great interest that has been shown recently in analyzing rates of reaction in the solid state will doubtless lead to a more rational basis for heat treatment. It has been usual to compare rate curves of the type shown in Fig. 7 with theoretical curves for first order chemical reactions. I think the authors have been wise in refraining from this. Obviously the process proceeds by nuclei formation and crystallization upon these nuclei. Sachs in Germany has recently analyzed rate curves upon this basis[28] and shown that the slow start of the reactions, which is anomalous when compared to curves of first order reactions, is in fact entirely normal. There is a real need for a close analysis of actual curves on the basis of the equations Sachs derives.

The authors' observations that inclusions occasionally act as nuclei for transformations may prove to be of practical importance. The crystallographic nature of the inclusion should determine its effectiveness in inoculating the unstable phase, for an inclusion showing a crystal symmetry similar to that of one or more of the decomposition products should be much more effective in inoculation than an inclusion without such crystalline similarity. This matter is one worthy of careful study. It might be possible to hurry transformation—when desired—by an incorporation of a proper inoculating inclusion, or to delay transformation—which practically would be of greater importance—by excluding or removing all such inclusions.

O. T. Marzke, Lansing, Mich.—In several of the specimens examined in my work on the precipitation of α from β brass, I noticed a duplex structure in the β field very similar to that shown in Figs. 44 and 45 of Smith and Lindlief's paper. I attributed it to an etching effect and continued etching until I was able to destroy it. I wonder whether anyone else has noticed this structure in β brass, and if it might not be due to a mixture of the β and β′ phases.

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[28] *Ztsch. f. Physik* (1932) **77**, 281.

R. M. Brick, New Haven, Conn.—Smith and Lindlief find that the temperature of the β transformation occurs at 570° C. Their micrographs show that this was found on polycrystalline material. Ageew and Kurdjumow, working with single crystals, apparently found the transformation at 583° C, judging from the few curves that were shown.

P. Wiest,[29] working with copper-silver alloys, found that the temperature of the transformation, copper solid solution to the two-phase copper and silver solid solutions, was different for polycrystalline and single-crystal alloys of the same composition. Could a similar effect of grain size explain the difference in the β transformation temperatures?

I. Obinata, Port Arthur, Manchuria (written discussion).—In the paper by Dr. Smith and Mr. Lindlief, and in that by Mr. Ageew and Mr. Kurdjumow, as well as in the recent work of Dr. Bradley and Dr. Jones,[30] I am glad to find that the existence of the intermediate β' phase, which I had detected in my previous work, is confirmed, though the experimental results differ somewhat in details with the authors.

Smith and Lindlief could not confirm the two breaks that I have found on the electrical-resistivity curves of the alloys on heating. I wonder whether the temperature of the furnace used by these authors was uniform enough to detect the two breaks, which should take place in succession in the narrow range of temperature of about 10° C. I agree with these authors that the β' phase is a metastable intermediate state during the eutectoid transformation, like martensite in the iron-carbon alloys, even if there appear two breaks on the resistivity curves on heating.

It is interesting to see in the paper by Ageew and Kurdjumow that the β' phase should be a sort of deformed cubic lattice. Recently Bradley and Jones arrived at a similar conclusion that the said phase is closely related to the face-centered α phase. I am carrying on further experiments on this subject, the result of which will be published in the *Memoirs* of the Ryojun College of Engineering.

The X-ray analysis of the α phase carried out by Smith and Lindlief has shown that the (400) line of the face-centered α phase disappears. Dr. G. Wassermann and I have recently found the same phenomena, in precision X-ray diagrams of this phase. The limiting value of the lattice constant of the α solid solutions is determined to be 3.6581Å. (20° C.).

N. Ageew, Leningrad, U.S.S.R. (written discussion).—The interesting new phase pointed out by Smith and Lindlief exists only in a narrow interval of temperature and time and it is only a coincidence that two quite different phases in their paper and in ours[31] were called β'. The phase β' in our paper is the metastable solid solution formed by quick cooling under conditions similar to formation of martensite in steel. This phase has been studied by many investigators and is well known by its acicular structure and a lattice quite different from the lattice of the β phase. The condition for the formation of this metastable phase is a low temperature, at which diffusion is not possible, but the rearrangement of the lattice occurs at a sufficiently rapid rate.

The phase β' of Smith and Lindlief is a new phase, not only studied, but also discovered by them. The formation of this phase at temperatures at which diffusion can proceed with a visible velocity leads us to suppose that Smith and Lindlief's β' phase is much closer in lattice structure to the stable phases α and γ than our phase β'.

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[29] *Ztsch. f. Physik* (1932) **74,** 225.

[30] A. J. Bradley and Phyllis Jones: An X-ray Investigation of the Copper-aluminum Alloys. Inst. of Metals *Advance copy* 625 (1933).

[31] See footnote on page 106.

It is not necessary now to consider the details of both papers. It may only be pointed out that if our investigation completes the research work in the domain of quenching of the aluminium bronze, the research by Smith and Lindlief not only attacks with a new tool the previously studied question of hardening of these alloys, but also points out the way for further research in this direction. I see in this the force and importance of the interesting and careful research of Dr. Smith and Mr. Lindlief.

A. J. Bradley, Manchester, England (written discussion).—I should like to congratulate the authors on their beautiful series of photomicrographs, showing the changes in the alloy containing 11.87 per cent Al produced by different heat treatments. For comparison, it would be interesting to have a series of X-ray photographs of this alloy after similar treatment. Do the authors consider acicular β obtained by quenching as in Fig. 5 to be equivalent to the β' phase of Obinata and other X-ray workers? If so, would they expect to find a difference in the X-ray photographs from this specimen and from the rosette-shaped particles which the authors have called β', and which are best shown in Fig. 28?

It has been our experience that filings taken from any alloy of composition 11 to 15 per cent Al, when quenched in water from a temperature high enough to prevent decomposition into $\alpha + \delta$, always give the same X-ray pattern. This corresponds to Obinata's β' phase, and is distinct from both the high-temperature body-centered β structure and the low-temperature α and δ phases. A photomicrograph from an alloy of the same composition and quenched in exactly the same way shows the typical acicular pattern. After annealing the powders at 500° C. for several hours and cooling in the furnace, the mixed patterns of α and δ are obtained, the corresponding photomicrographs showing eutectoid with either primary α or primary δ.

It is remarkable that our β' X-ray pattern is so very similar to the α pattern. It might easily be mistaken for a mixture of α with another phase, were it not for the absence of lines to correspond with the lines 200, 400, and 331 of the face-centered pattern. The extreme fuzziness of the lines is, however, in striking contrast with the comparatively sharp lines of the α pattern.

G. Kurdjumow, Dnjepropetrowsk, U.S.S.R. (written discussion*).—It is especially interesting to note that the authors were able to observe decomposition of the β phase at different temperatures and the differences in the course of the decomposition.

It has already been shown by Obinata[32] that the lattice of "acicular β" differs from the lattice of the stable β phase at high temperatures and has an X-ray diffraction pattern with many lines. Obinata designates this phase as β' and assumes its existence even at high temperatures, so that the eutectoid decomposition should take place according to the expression $\beta \rightleftharpoons \beta' \rightleftharpoons \alpha + \delta$. The heating curve that was obtained in the work of Ageew and myself, and the "electric resistance-temperature curves" of Smith and Lindlief, show, however, that there is no new phase in the equilibrium diagram. Further, from the pole figures of some surfaces of the new lattice and from the powder diagram it can be concluded[33] that this lattice represents a somewhat distorted cubic lattice and a similar orientation, such as that of martensite or α iron to austenite,[34] that of α tin bronze to the β phase[35] and that of the

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* Translated from the German.

[32] I. Obinata: *Mem.* Ryojun College of Engineering (1931) **3,** 285.

[33] N. Ageew and G. Kurdjumow: See footnote on page 106.

[34] G. Kurdjumow and G. Sachs: *Ztsch. Phys.* (1930) **64,** 325.
R. F. Mehl, C. S. Barrett and D. W. Smith: *Trans.* A.I.M.E. (1933) **105.**

[35] J. Jsaitschew and G. Kurdjumow: *Metallwirtschaft* (1932) **11,** 554.

α brass to β brass.[36] The new lattice can be considered as a distorted lattice of the α Al bronzes.

In our work we retain the Obinata designation β' for this lattice. Here I would call this phase "acicular β" in order not to confuse it[37] with the new phase β' found by Smith and Lindlief. The lattice determination of the "acicular β" has not been done satisfactorily (the indication of the powder diagram given by Obinata is contradictory to the pole figures obtained by Ageew and myself) and it must be considered as one of the next tasks because of its great importance in the problem of the mechanism of transformations in the solid state.

The authors of the paper under discussion came to the same conclusion regarding the nature of the acicular β on the basis of their microscopic results, and consider this phase as an α phase supersaturated with aluminum. They also tried to find confirmation of this conclusion by determining the lattice dimensions, and found the spacing of the lattice plane intervals. They call attention to the fact that the line (100) of the face-centered α lattice disappeared on the powder picture of the 11.87 per cent alloy; in addition new lines are seen. This can be explained by the fact that it is not a case of a cubic, but a somewhat distorted cubic lattice. Our X-ray pictures show the same lines that are given in Table 6. They also show, like the photograms of Obinata, a number of lines some of which are not weak. The powder diagrams of Smith and Lindlief were made from the sample that had been quenched in the salt bath at 375° and were heated at this temperature for 72 hr. before quenching in water. According to tests made with Ageew, the lattice of the acicular β decomposes with an appreciable velocity at this temperature. Then the α phase appears and also the line (100). For this reason it must be expected that if the acicular β forms during heating at 375°, it would also be subject to gradual decomposition. But we see that no (100) line is present. This fact might possibly be explained otherwise, but it is not precluded by the following hypothesis. The decomposition of the β phase does not take place at all at the temperature of 375°; the formation of the acicular β takes place only on further quenching in water. Therefore it is possible that here also, as in austenite, there is a temperature interval in which the β phase could remain undecomposed for a long time.[38] But we have as yet no experimental data in this direction. In regard to the mechanism of the formation of acicular β we now have the idea, according to which it consists in the uniform lattice transformation of individual regions of the β lattice into the lattice of the α phase, as is the case in the formation of martensite.

TABLE 6

11.87 PER CENT ALLOY KEPT 72 HR. IN SALT BATH AT 375° AND QUENCHED IN WATER (SMITH AND LINDLIEF), ANGSTROMS	12.6 PER CENT ALLOY QUENCHED IN WATER FROM 1000° (AGEEW AND KURDJUMOW), ANGSTROMS
2.250	2.22
2.125	2.09
2.040	2.01
1.953	1.93
1.295	1.29
1.110	1.11
1.059	1.06

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[36] M. Straumanis and J. Weerts: *Ztsch. Phys.* (1932) **78,** 1.

[37] Possibly it might be more correct to designate "acicular β" by α' as was done by Öhman [*Jnl.* Iron and Steel Inst. (1931) **123,** 445.] for indicating the tetragonal lattice of martensite.

[38] See, for example, H. Hanemann and H. Wiester: *Arch. Eisenhüttenwesen* (1931–32) **5,** 377; H. Wiester: *Ztsch. Metallkunde* (1932) **24,** 276.

But as this change in atomic arrangement takes place at a high velocity[39] and at temperatures at which diffusion is very slow, a supersaturated solid solution of aluminum in the α lattice forms. The supersaturation causes the distortion of the α lattice.

As used by Smith and Lindlief, the method of investigating the eutectoid decomposition at different temperatures, and the wonderful photomicrographs obtained by them, permit the establishment of the new fact that the decomposition of the β phase takes place in a temperature region by a new intermediate state. The authors use β' to designate this phase. It also was shown that this phase is unstable and forms only as an intermediate state. It is interesting that an apparently similar intermediate phase also forms during the decomposition of the β phase of copper-tin alloys, which I was able to observe in work with Isatschew and Buyakow in Leningrad. With suitable cooling it was possible to obtain the *β phase at room temperature.* Then the decomposition of the β phase was studied with poly and single crystals.

Thus it was found that the decomposition of the β phase into $\alpha + \delta$ does not take place directly, but in a certain temperature interval, through an intermediate phase. The lattice of this phase is hexagonal and has a definite orientation (with four positions) in relation to the lattice of the mother phase. The nature of this phase is not yet evident; it still leaves open the question of the concentration ratios in this phase. The photomicrographs of this phase, as well as those of the β' copper-aluminum, differ from those of the martensitic intermediate state. It also is clear that diffusion can not play a part in the formation of this phase.

One can obtain decomposition of the β phase of copper-tin bronze even during cooling, by quenching in a certain way. This forms an "acicular structure." The powder photograms in this case show a line system that is very similar to the acicular β copper-aluminum.

The mechanism of the formation of α needles in the region between 535° and 400° also is not clear to me. The authors state that the quantity of α needles always increases with decreasing temperatures of the salt bath until the acicular β forms. They further conclude that these α needles must be supersaturated with aluminum. Is it not possible that the mechanism of the formation of the α needles may be the same as in the formation of acicular β? If so, the supersaturated α lattice must naturally decompose immediately after its formation, because it is found at temperatures at which it can decompose rapidly. (Decomposition of the acicular β takes place rather rapidly even at 400°.) If the mechanism is as indicated, the formation of α needles must proceed through the β intermediate state. It also is possible that the decomposition of the β phase in the temperature region of 535° to 400° can take place in two different ways: (1) through β' and (2) through the other intermediate state, acicular β.

According to the last investigations, therefore, it appears that the transformations at the eutectoid are rather complicated. But it can be seen that the fundamentals of the transformation processes are essentially very similar with different eutectoid alloys. It can be concluded that the eutectoid decomposition can take place in at least three ways:

1. The transformation of the β phase takes place with great subcooling, and consists only in the mechanical reconstruction of the individual lattice regions without a change in concentration. The mechanics of the change itself can be described[40]

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[39] According to the experiments of H. Wiester, who observed the formation of martensite in steel in a film photogram, the time required for the formation of a martensite needle is less than 1/20 second [*Ztsch. Metallkunde* (1932) **24,** 276].

[40] A. Ivensen and G. Kurdjumow: *Vestnik Metallopromischlennosti* No. 9 (1930).
G. Kurdjumow and G. Sachs: *Ztsch. Phys.* (1930) **64,** 325.
R. F. Mehl, C. S. Barrett and D. W. Smith: Reference of footnote 34.

on the basis of orientation determinations. The resultant intermediate state can remain undecomposed for a long time, if diffusion is extremely slow. The intermediate lattice closely approximates the lattice of a crystal type of the eutectoid and can be considered as a supersaturated unstable solid solution. The decomposition of this intermediate phase takes place on annealing with the separation of one constituent; then the intermediate lattice approaches the lattice of a crystal type, retaining the orientation of this crystal type. The state of the separated constituent is not yet clear.[41]

2. The decomposition of the β phase also takes place with great subcooling but in a temperature range in which diffusion can act. Here also, decomposition takes place through an intermediate state that differs from the first intermediate state. Very little can be said at present in regard to the mechanics of the formation of this phase and its nature; further experiments are necessary. It also is possible that the decomposition in this temperature region may pass through the first intermediate lattice,[42] which decomposes very rapidly by diffusion at these temperatures. It is not impossible that the transformation may pass through both intermediate phases.

3. With moderate subcooling decomposition takes place directly with the formation of nuclei of both crystal types of the eutectoid and their further growth.

C. S. Smith (written discussion).—Many of the discussions have criticized our use of the term β' for the intermediate transitional phase that occurs in the form of rosette-shaped particles. The objection is based mainly on Obinata's original assignation of the term β' to the form we have called "low-temperature α." Unfortunately we did not encounter Obinata's work until our own was well advanced and did not deem the change essential, particularly since Obinata was of the opinion that his β' had a stable existence in the equilibrium diagram, which we have refuted. In my own opinion, low-temperature α should be called α', following Dr. Kurdjumow's suggestion, rather than β', since it is much more closely related to the α phase than to β.

The suggestion by Dr. Mathewson that the structure we have called β' is merely recrystallization of β is most interesting. However, I do not think that this is sufficient explanation, since β' forms from β at comparatively high temperatures even on furnace cooling under conditions where there is no strain. The acicular markings indicating strain are formed only on quenching or at a lower temperature than those at which β' is first formed. Morever, when the β' transformation is completed, the entire original β grain consists of β', and if it were merely recrystallization it would have resulted in a change of orientation of the grain as a whole, for which there would seem to be no reason. The acicular markings developed less readily in β' than in β and do not appear at all in β' from which the excess of α has been precipitated (see, for example, Figs. 26 and 41). I expect that an alloy of sufficiently high aluminum content would change to a β' with no acicular markings, which might have a considerable degree of stability. We hope to undertake in the future a study of the reaction in alloys of several different compositions.

Dr. Mehl's observation that the β' is definitely orientated in relation to the parent β is obviously correct. The Widmanstätten form is particularly well developed in alloys containing tin (Fig. 62) but it is noticeable in the pure aluminum-copper alloys. I imagine that the β' particles grow almost equally in three directions, and in this respect the analogy with γ precipitation from β brass is correct. β' seems to have not only a related orientation but exactly the same orientation throughout a given β grain. Most precipitates occur in a limited number of orientations; this in one only.

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[41] For iron-carbon, see G. Kurdjumow: *Ztsch. Phys.* (1929) **55**, 187; *Archiv f. Eisenhüttenwesen* (1932–33) **6**, 167. F. Wever: *Ztsch. Metallkunde* (1932) **24**, 270. We have too few experimental data on the decomposition of "acicular β."

[42] According to Wever (*op. cit.*) the transformation of austenite in this temperature range goes through the tetragonal intermediate lattice.

I was so fully aware that the α plates in Figs. 29 and 30 were straight plates with frequent changes of orientation that I considered the *apparent* curvature at low magnification an interesting fact worthy of note.

The excellent work of Dr. Mehl on the orientation relations on solid transformations, and the large crop of work by others that he has inspired, made us hesitant to attempt such studies in the present case. We have also avoided any attempt at a mathematical study of the rates of reaction, and, in fact, rather regret our attempts to develop a theory of β' formation until more data as to its mode of occurrence are available.

The remark by Mr. Marzke to the effect that structures similar to the $\beta + \beta'$ structure observed in the copper-aluminum system can also be obtained under some conditions in the copper-zinc system indicates that it is due to the same cause. It is possible that the metastable β' phase of the copper-aluminum system has the same structure as the β except for a regular instead of random arrangement of atoms.

I do not think that the discrepancy between Ageew and Kurdjumow's work and my own on the temperature of the eutectoid transformation can be explained on the basis of crystal size, as Mr. Brick suggests. As stated in footnote 22, there is not a great difference in the rate of transformation between normal polycrystalline material (about 0.8-mm. dia.) and single crystals measuring ½ in. square.

Dr. Obinata's remarks are most interesting. I do not think our results are concordant with the stable formation of β'. If this phase had been formed with reasonable speed it certainly would have appeared in microsamples quenched after long periods at 568° C. (Fig. 3). The sample used for determining the eutectoid temperature by electrical conductivity measurements was bent into a grid measuring 1½ by ¾ by ¼ in. This was placed inside a heavy copper tube of 1-in. inside diameter with ½-in. walls. It is impossible that there could have been an appreciable temperature difference along the specimen or that the thermocouple indicated a temperature different from that of the specimen. Additional confirmation of the absence of β' in the equilibrium diagram is given by the dilatometric curves of Ageew and Kurdjumow.

Dr. Ageew considers the new β' phase to be closer in lattice structure to the stable phases α and γ than is the low-temperature α (acicular β). I have come to regard our β' phase as much more similar to β than to either α or γ.

Many comments have been made on the X-ray study mentioned as a footnote in the original paper. Most of the study was based on microscopic evidence; and no particular claim for accuracy is made for the X-ray studies. In reply to Dr. Bradley's question, I believe the acicular β to be similar to "low-temperature α" and identical with the β' phase of Obinata. In my opinion, this should be called α', and I believe my own β' phase (the "rosette-shaped" particles) to be totally different from the acicular form. Rosette-shaped β' often decomposes on quenching to an acicular form but it seems to be more stable than ordinary β, particularly when it has had an opportunity to precipitate the excess α, and I believe that true β' could be retained at room temperatures for examination. My guess is that it is identical with β except for a regular arrangement of atoms, and in that way the analogy with the copper-zinc β phase is close.

I am in almost complete accord with Dr. Kurdjumow's statements except possibly regarding the connection between the α needles forming at high temperatures and acicular β forming at low. I believe that "acicular β" forms very rapidly at 375° C. (probably with an intermediate β' phase, although this cannot be identified microscopically). I consider that the alpha that forms at higher temperatures, although supersaturated in relation to delta, is in equilibrium with β' (although, of course,

β' is not an equilibrium phase) and therefore the α needles are themselves quite stable as long as β' rather than δ is the phase with which they are in contact.

Although acicular β will decompose rapidly on *reheating* to 400° C., the rate of decomposition is evidently less on direct *cooling* from the β zone to 375° C., and even after 32 days at 375° C. (see Fig. 40) the amount of decomposition is relatively small. The sample used for the X-ray diffraction pattern had been held 72 hr. at 375° C., following cooling from 900° C., and the microscope showed it to resemble Fig. 40 except for the absence of precipitation of undoubted α and γ in the grain boundaries.

Is it not possible that acicular β results from the supersaturation of α with δ and is formed by the decomposition of this supersaturated α of face-centered cubic structure rather than from the decomposition of β or β' body-centered cubic structure? Looked at in this way the mechanism of decomposition of an alloy of eutectoid composition is roughly as follows: β first decomposes to β', and subsequently or simultaneously α in large quantities appears, this α containing far more aluminum than is normally possible. With falling temperature the amount of α increases and β' decreases. At a certain stage the structure will consist practically entirely of α, supersaturated with aluminum but still of the normal face-centered cubic structure. At low temperatures, after all β' has disappeared this unstable α commences to relieve its supersaturation, and does so through the intermediate stage of the acicular β, which has a distorted face-centered cubic structure. According to this conception, the parent of acicular β is a transitionally stable supersaturated α and not either β or β'.

Segregate Structures of the Widmanstätten Type Developed from Solid Solutions of Copper in Zinc

By M. L. Fuller* and J. L. Rodda,* Palmerton, Pa.

(New York Meeting, February, 1933)

In connection with an investigation in this laboratory on the high-zinc side of the copper-zinc system, it was observed that well developed segregate structures of the Widmanstätten type were formed when a secondary phase precipitated from the solid solution of copper in zinc. This paper presents an analysis of the crystallographic relationship between the segregate and the solid solution matrix.

The data to be presented are an interesting addition to the literature on segregate structures in that the plane of segregation is one of the less densely populated planes. In agreement with the generalization of C. H. Mathewson and D. W. Smith[1] the plane of segregation in the matrix contains the direction of closest atomic packing of the lattice. Furthermore, the matrix and the segregate are both hexagonal close-packed, which has not been reported hitherto in the literature.[2] The increasing commercial importance of zinc alloys containing copper makes this fundamental study of value to the metallography of zinc alloys.

ZINC-RICH COPPER-ZINC ALLOYS

Copper enters into solid solution with zinc to at least 1.8 per cent at 400° C., according to W. M. Peirce.[3] The solubility is less at lower temperatures. Thus a solid solution of copper in zinc, saturated at an elevated temperature, will precipitate the excess copper in a separate phase at a lower temperature, conditions of concentration, time, and temperature being suitable.

The nature of these two phases has been established by the X-ray method of crystal analysis. Westgren and Phragmén[4] and also Owen and Preston[5] have shown that the solid solution eta (η) is of the substitutional type with copper atoms replacing zinc atoms on the hexagonal close-packed zinc structure in a chance distribution. Recent measurements in this laboratory with a Bohlin precision camera have shown that the solution of copper causes a decided decrease in axial ratio. The change from pure zinc to the solid solution of copper in zinc in a 1 per cent copper alloy is as follows:

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* Investigator, Research Division, The New Jersey Zinc Co.

[1] C. H. Mathewson and D. W. Smith: *Trans.* A. I. M. E. (1932) **99,** 264–273.

[2] An excellent summary of the published data on Widmanstätten structures is given by C. H. Mathewson and D. W. Smith: *Op. cit.*

[3] W. M. Peirce: *Trans.* A. I. M. E. (1922) **68,** 767–795.

[4] A. Westgren and G. Phragmén: *Phil. Mag.* (1925) **50,** 311–341.

[5] E. A. Owen and G. D. Preston: *Proc.* Phys. Soc. (London) (1923) **36,** 49–66.

	a_0	c_0	c/a (Axial Ratio)
Pure zinc	2.660 ± 0.0005Å	4.938 ± 0.001Å	1.856
Solid solution	2.664 ± 0.0005Å	4.896 ± 0.001Å	1.838

The atomic arrangement in the epsilon (ϵ) phase which precipitates from the η solid solution has been shown also to be hexagonal close-packed. The axial ratio in the case of ϵ is much lower than in that of η. The ϵ phase saturated with zinc at 200° C. has the following dimensions:[6]

$$a_0 = 2.762 \pm 0.003\text{Å} \quad c_0 = 4.308 \pm 0.005\text{Å} \quad c/a = 1.560$$

It has not been possible to establish whether the constituent atoms in ϵ are arranged at random on the hexagonal close-packed structure, as in a solid solution, or whether they occupy definite positions. Owen and Preston[7] suggested a possible arrangement but were able to offer no proof, because of the near equivalence in X-ray scattering power of copper and zinc. Westgren and Phragmén[8] found that structurally similar phases in the silver-zinc and gold-zinc systems gave no evidence of anything but chance disposition of the constituent atoms and drew the corollary that such also was the case in the copper-zinc system.

The classification of ϵ and η as "ideal solid solutions" by Westgren and Phragmén is probably the best to be made from the information available.

The precipitation of ϵ from η is readily accomplished but the formation of well developed segregate structures requires special and careful heat treatment.

PREPARATION OF ALLOYS

The two alloys used in this investigation were part of a group prepared by Gerald Edmunds, of this laboratory, to whom we are greatly indebted for the specimens used in this work. The alloys were originally prepared for a study of the solid solubility limits of copper in zinc in the presence of small amounts of magnesium and iron. The base metal used was a C.P. grade of zinc and the total added magnesium plus iron was less than 0.04 per cent.

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[6] These measurements were made in this laboratory using the powder diffraction apparatus described by W. P. Davey in the *General Elec. Rev.* (1922) **25**, 565.

[7] Reference of footnote 5.

[8] Reference of footnote 4.

One alloy contained 1.54 per cent copper by analysis. It was cast from 475° C. into molds at approximately 210° C. (size of slab, 3 by 9 by ⅝ in.). The slab was annealed 24 hr. at 375° C. then rolled at 180° to 200° C. to 0.060 in. The rolled strip was annealed 48 hr. at 400° C., insuring complete solution of all copper. A final annealing treatment of 14 days at 200° C. followed by quenching caused precipitation of the excess copper as ϵ.

The second alloy analyzed 1.69 per cent copper. The treatment of this alloy was the same as for the first alloy except for the final annealing treatment, which was seven days at 200° C.

Fortunately the rolling and annealing treatments yielded crystals, approximately 0.5 by 0.06 in. in cross-section, ideal for X-ray and microscopic study.

Determination of Plane of Segregation

The method used in determining the plane of segregation is the same as that so successfully used by R. F. Mehl and his colleagues[9] in a series of papers on segregate structures. Starting with the polished microspecimen, an X-ray determination of the orientation of a single matrix crystal is made and planes or directions in the lattice are sought which could give rise to the segregate structures observed under the microscope.

Preparation of Microsections.—For the initial study the microsection was polished on a cross-section parallel to the rolling direction. The results of the first study indicated that the interpretation would be facilitated if an additional plane of polish were examined.

In the preparation of the microsection, the final polishing was carried out by the method previously described by one of the writers.[10] The specimens were etched approximately one second in a solution of 20 grams CrO_3 and 1.5 grams Na_2SO_4 in 100 c.c. water.

Measurement of Photomicrographs.—The angles of the segregate traces were measured to the nearest degree with reference to a fine scratch produced with a drawn quartz point. The length of each trace was measured, in order that more weight might be given to the longer traces, which represent a larger proportion of the entire segregate and whose directions are more accurately measurable.

Upon each plane of polish a total of 750 to 1200 traces were measured over an area of 50 to 75 sq. cm. at 500 dia. Frequency plots were prepared in which the measured angles were plotted as abscissas and the sum of the trace lengths for each angle as ordinates.

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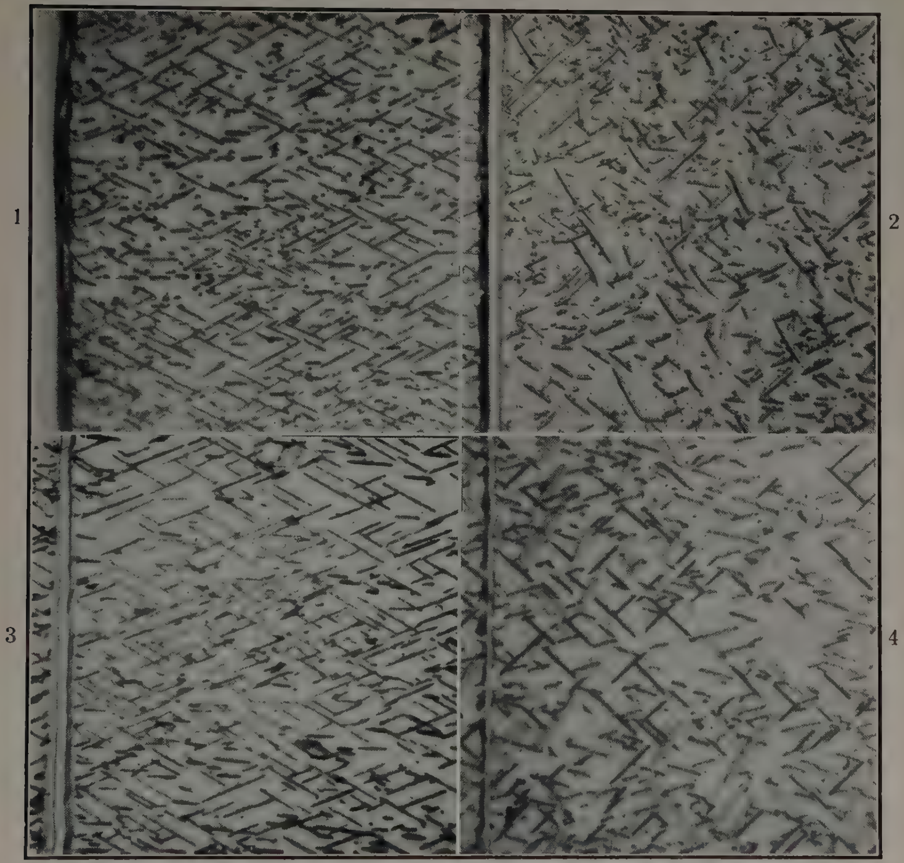
[9] R. F. Mehl and C. S. Barrett: *Trans.* A. I. M. E. (1931) **93,** Inst. Metals Div., 78–122.

R. F. Mehl and O. T. Marzke: *Ibid.*, 123–161.

R. F. Mehl, C. S. Barrett and F. N. Rhines: *Trans.* A. I. M. E. (1932) **99,** 203–233.

[10] J. L. Rodda: *Trans.* A. I. M. E. (1932) **99,** 149–158.

Orientation Determination by X-ray Method.—The matrix crystals were sufficiently large so that a determination of their orientation with respect to the plane of polish and reference scratch was very easily performed. The method used was the stationary-oscillating film method proposed by W. P. Davey[11] and outlined in detail by T. A. Wilson.[12] Molybdenum $K\text{-}\alpha$ X-rays, film radii of 7.70 and 8.45 cm., and a 5-in. stereographic net were used in carrying out the method.



FIGS. 1–4.—SEGREGATE STRUCTURES IN ZINC-COPPER ALLOYS. ×500.
Fig. 1.—1.54 per cent Cu alloy, original plane of polish.
Fig. 2.—1.54 per cent Cu alloy, second plane of polish.
Fig. 3.—1.69 per cent Cu alloy, original plane of polish.
Fig. 4.—1.69 per cent Cu alloy, second plane of polish.

Results.—The alloy containing 1.54 per cent copper, whose preparation and heat treatment were described earlier in this paper, was the first to be examined. Fig. 1 shows a photomicrograph of this specimen in which three principal directions of segregate figures are present. Previous microscopic observations indicated that the segregate takes the form of plates. Assuming that this form of segregate structure obtains in the present case, the needlelike figures in the photomicrograph (Fig. 1) are traces of plates intersecting the plane of polish. Planes of the form {10.0} or {11.0}, consisting of three families each, immediately suggest themselves as planes of the matrix upon which the plates form. In order definitely to identify the plane of segregation, however, it is necessary to know the orientation of the matrix crystal.

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[11] W. P. Davey: *Phys. Rev.* (1924) **23,** 764.

[12] T. A. Wilson: *General Elec. Rev.* (1928) **31,** 612–621.

The orientation of the matrix crystal of Fig. 1 is shown on the stereographic projection, Fig. 9. The plane of polish of the microspecimen is the plane of projection and the reference scratch shown on the photomicrograph is indicated on the projection by the vertical diameter of the primitive circle. The traces of the segregate plates are indicated by the diameters marked *W*, the positions plotted being the weighted averages in the three groups of positions found. The distribution of the measured directions of segregate traces is graphically shown on the frequency plot, Fig. 5.

Examination of the stereographic projection revealed that {10.0} or {11.0} could not possibly be planes of segregation and that choice must be made among the planar forms having more than three families. Confining the search to planes of relatively low indices, it was found that selection must be made among {10.3}, {10.4} and {10.5}. With the stated orientation of matrix crystal, these planes give rise to three pairs of traces for each form of planes, the two members of each pair being separated only a few degrees from one another. On the basis of this determination the {10.4} plane is the plane of segregation. It is evident that instead of three directions of traces there are, in fact, three pairs of two directions each.

In order to verify this analysis the specimen was repolished at such an angle that one of the {10.4} planes was nearly in the plane of polish. Upon such a plane of polish the segregate should show five traces and one plate.

Fig. 2, a photomicrograph of the new section, confirms the analysis made upon Fig. 1, since it shows plates nearly parallel to the plane of polish and five distinct directions of segregate traces. The angular distribution of the traces is shown on the frequency plot of Fig. 6 and the weighted average of each of the five groups of directions is drawn upon the stereographic projection of the matrix orientation, Fig. 10. This projection establishes the fact that there are six orientations of plates but it is difficult to decide among the {10.3}, {10.4} and {10.5} planar forms. Part of this difficulty is due to inability to plot the traces accurately on the projection and to measure the position on the photomicrograph of those planes which make small angles with the plane of polish.

In order to identify the plane of precipitation more conclusively, the second alloy (1.69 per cent Cu) was examined.

The photomicrograph, frequency plot, and stereographic projection are given in Figs. 3, 7 and 11, respectively. The orientation shown on the projection happened to be very similar to that of the first case (Figs. 1, 5 and 9) and again the {10.4} traces are most nearly parallel to the segregate traces.

Using the method of the stereographic projection, an orientation of the solid solution matrix was found which would give a greater separation in the traces of the planes {10.3}, {10.4} and {10.5} than was obtained in the three cases discussed above. Accordingly, the crystal of the 1.69 per cent alloy was repolished at an angle such that this orientation with respect to the plane of polish was produced. The corresponding photomicrograph, frequency plot, and stereographic projection are shown as Figs. 4, 8 and 12, respectively.

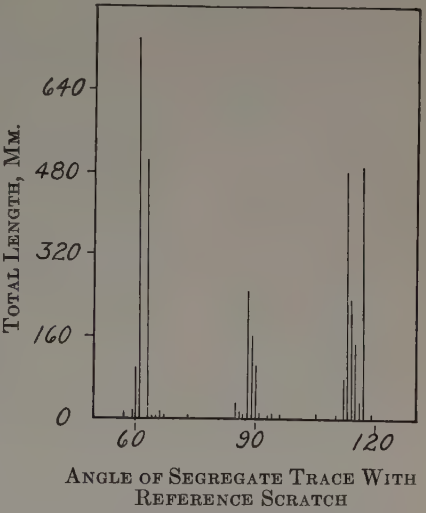

Fig. 5.—Frequency plot of segregate traces corresponding to Fig. 1.

In four of the six orientations, the segregate traces almost coincide with those of the {10.4} planes. The other two cases show poor agreement with {10.4}, which is very probably caused by these planes appearing as elongated plates instead of needlelike traces, making it difficult to select the true trace. This is due to the fact that these two plates make small angles (less than 20°) with the plane of polish. Furthermore, in plotting, a small error in locating the stereographic projections of these

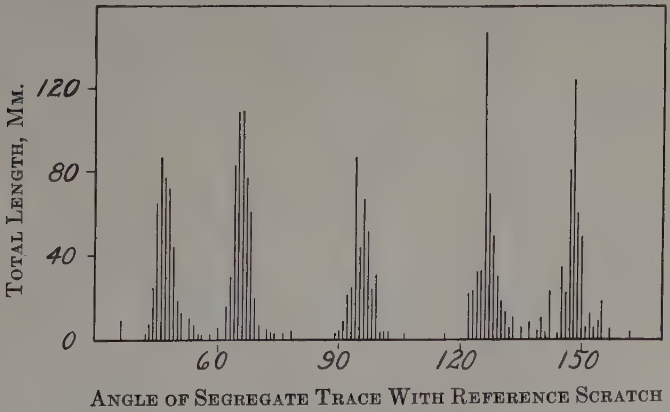

Fig. 6.—Frequency plot of segregate traces corresponding to Fig. 2.

two planes makes a large error in the location of the traces in the plane of polish.

The data presented above are sufficient to establish the fact that planes of the form {10.4} of the η solid solution are the ones upon which plates of ϵ form. Some of the experimental data are in better agreement with planes of the form {10.3} or {10.5} as planes of segregation but in none of the four cases examined does lack of evidence for {10.4} point consistently to {10.3} or {10.5}.

To determine the identity of the matrix plane of segregation is only a partial solution of the crystallographic problem presented by these structures. The final and experimentally most difficult step is to determine the orientation of the segregate relative to the matrix.

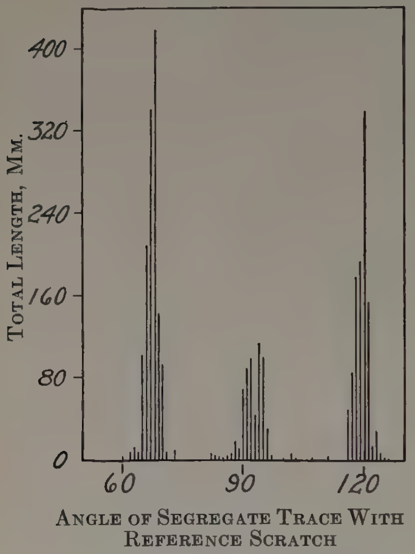

Fig. 7.—Frequency plot of segregate traces corresponding to Fig. 3.

Orientation of the Segregate Relative to the Matrix

In the study of segregate structures in the silver-aluminum alloys by Mehl and Barrett,[13] the relation of the precipitated γ phase to the δ solid solution was definitely determined by an ingenious method. A preferred orientation of the homogeneous solid solution was produced by wire drawing, after which precipitation was caused to take place by suitable annealing.

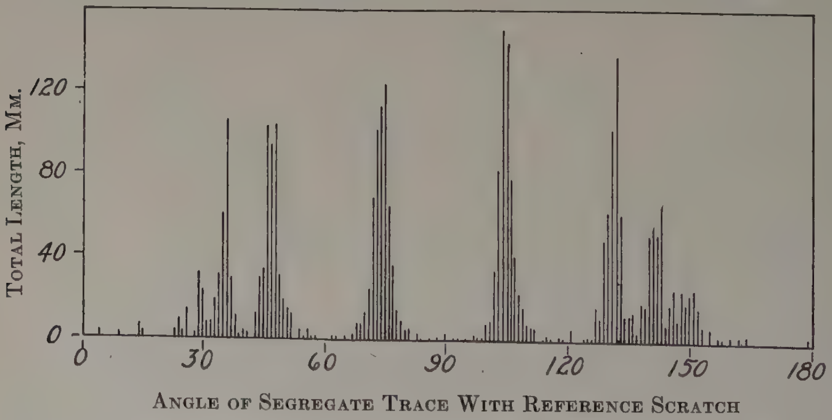

Fig. 8.—Frequency plot of segregate traces corresponding to Fig. 4.

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[13] First reference of footnote 9.

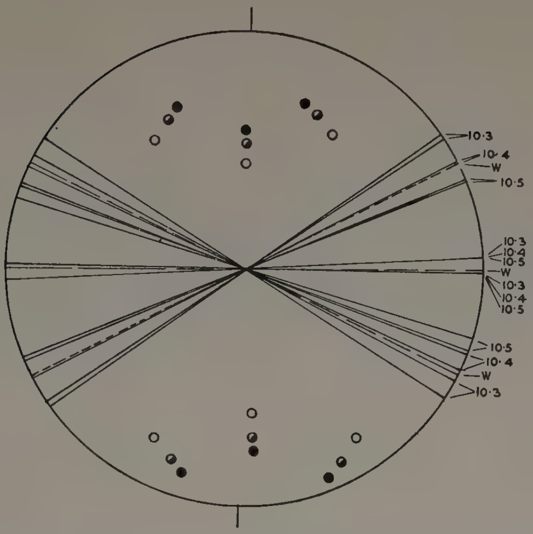

FIG. 9.—STEREOGRAPHIC PROJECTION UPON PLANE OF POLISH OF FIG. 1.
○ (10.3) planes, ◒ (10.4) planes, ● (10.5) planes.

Full lines, traces of matrix planes; dashed lines, traces of segregate plates; dotted lines, coincident traces of matrix planes and segregate plates.

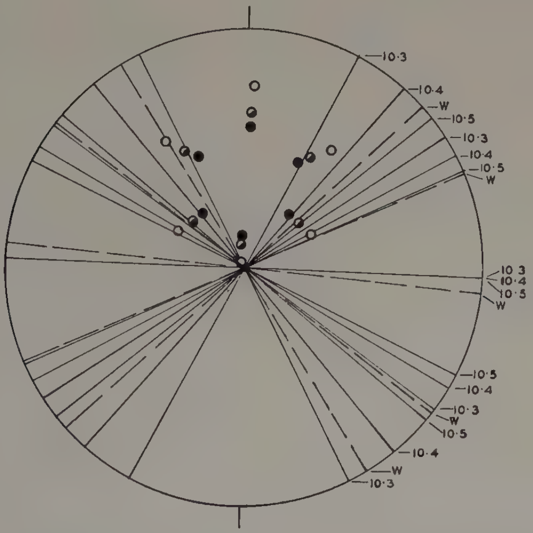

FIG. 10.—STEREOGRAPHIC PROJECTION UPON PLANE OF POLISH OF FIG. 2.
○ (10.3) planes, ◒ (10.4) planes, ● (10.5) planes.

Full lines, traces of matrix planes; dashed lines, traces of segregate plates; dotted lines, coincident traces of matrix planes and segregate plates.

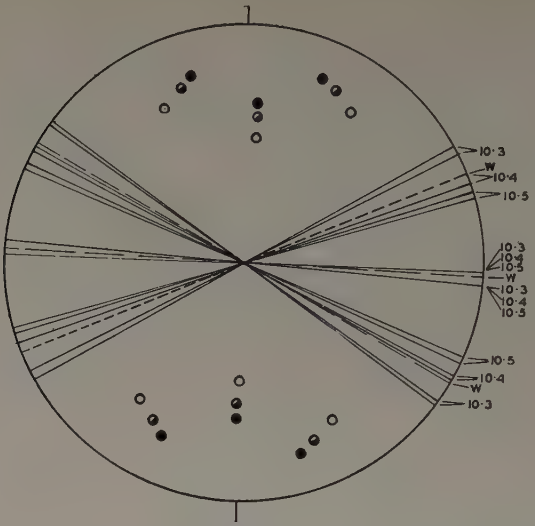

FIG. 11.—STEREOGRAPHIC PROJECTION UPON PLANE OF POLISH OF FIG. 3.
○ (10.3) planes, ◒ (10.4) planes, ● (10.5) planes.

Full lines, traces of matrix planes; dashed lines, traces of segregate plates; dotted lines, coincident traces of matrix planes and segregate plates.

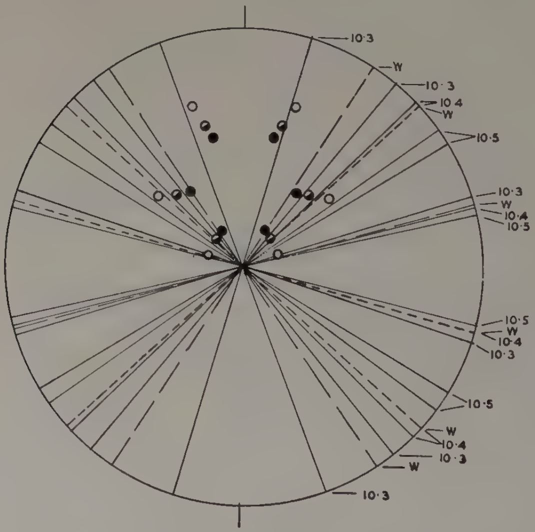

FIG. 12.—STEREOGRAPHIC PROJECTION UPON PLANE OF POLISH OF FIG. 4.
○ (10.3) planes, ◒ (10.4) planes, ● (10.5) planes.

Full lines, traces of matrix planes; dashed lines, traces of segregate plates; dotted lines. coincident traces of matrix planes and segregate plates.

This treatment resulted in mutually related fiber structures of the segregate and the matrix. These fiber structures were analyzed by a suitable X-ray method.

Experimental Procedure

Repeated attempts were made in the present investigation, with the cooperation of R. L. Wilcox, to produce a condition in rolled copper-zinc alloys similar to that obtained by Mehl and Barrett. The experiment was unsuccessful, since it proved to be impossible to detect the diffraction pattern of the ϵ precipitate. This lack of sensitivity was due, probably, to the small concentration of precipitate in these alloys.

Attempts with polycrystalline metal having failed, some experiments with single matrix crystals were tried. A crystal displaying plates of segregate in the plane of polish was selected for study (Fig. 2). An oscillating crystal pattern was taken, using filtered molybdenum characteristic X-rays with the matrix crystal oscillating about a normal to a (11.0) plane. Upon the equator line were recorded X-ray reflections from (10.2), (10.3), (10.4) and (10.5) planes of the matrix and (10.2) and (10.3) planes of the segregate.

On the assumption that the two reflections from the segregate came from the same orientation of ϵ crystals, the evidence would indicate that a normal to a (11.0) plane in each of the reflecting ϵ crystals is parallel to a normal to a (11.0) plane of the matrix. However, since six groups of crystals of unknown orientation are present, it is not possible to be certain of the correctness of this assumption.[14]

In the theoretical discussion that follows, it appears that the above assumption is probably correct, since with its aid a logical and reasonable picture of the relation between segregate and matrix is developed.

Theoretical Discussion

R. F. Mehl and his coworkers have proposed and offered experimental evidence to support the theory that the formation of segregate plates requires the atomic arrangement and interatomic distances on the mutual planes of separation of matrix and segregate to be very similar. On the basis of this theory and on the assumption that the closest packed direc-

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[14] In order to obtain definite evidence to uphold this assumption, the stationary-oscillating film method was tried, but met with failure. These attempts were unsuccessful since the reflections from ϵ were not recorded on the oscillating film. In this method of X-ray examination, the reflected rays are always sharply recorded on the stationary film but usually are diffusely recorded on the oscillating film owing to lack of perfection in the crystal. In the present case sharp records on the oscillating film require, in addition to perfection of the matrix crystal, perfection in the mutual orientation of cooperating plates of segregate. Since the reflections from the ϵ plates were initially weak, a tendency toward diffuse registry on the oscillating film left no detectable record.

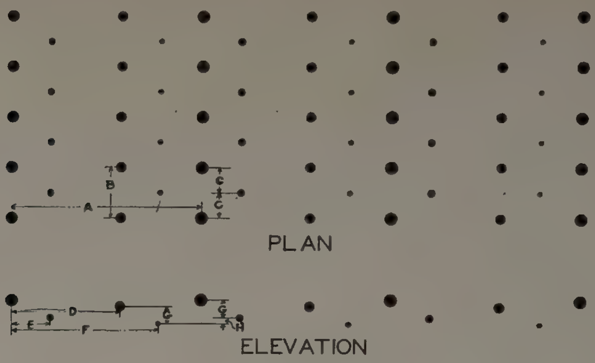

FIG. 13.—ATOMIC ARRANGEMENT IN PLANES OF FORM (10.4).

Phase	Dimensions							
	A	B	C	D	E	F	G	H
η	10.45Å	2.664	1.332	6.112	2.038	8.130	1.081	0.360
ε	10.49	2.762	1.381	6.123	2.181	8.304	0.982	0.327

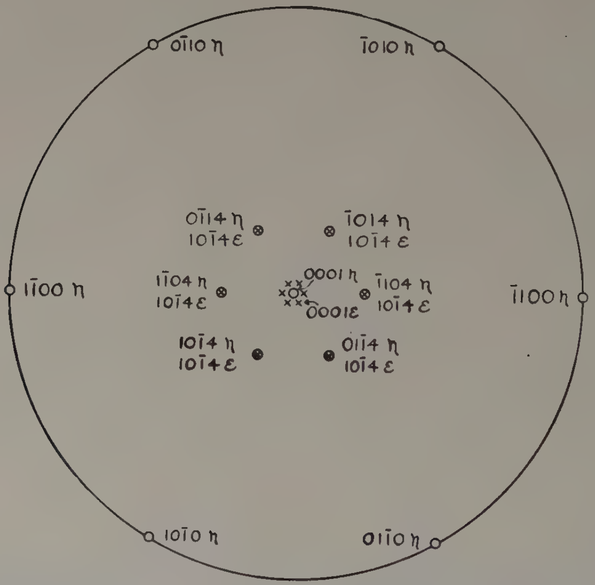

FIG. 14.—STEREOGRAPHIC PROJECTION OF A MATRIX CRYSTAL WITH SIX SEGREGATE CRYSTALS.

○ Projections of matrix planes.
× Projections of segregate planes.
⊗ Projections of coincident matrix and segregate planes.

tions in the two crystals are in common, a (10.4) plane of ϵ was considered[15] to be the one most probably parallel to the (10.4) segregation plane of the matrix.

The atoms in either (10.4) plane are disposed on a rectangular network, successive layers of these planes being built up in a similar manner in each phase. Fig. 13 shows the atomic arrangement in these two phases as plan and elevation views on a (10.4) plane, showing four layers in each figure. The table of interatomic distances accompanying Fig. 13 shows the close agreement between these two planes. No attempt has been made to distinguish between copper and zinc atoms on this diagram, since the two kinds of atoms are considered to be disposed at random in either phase.

Assuming that a (10.4) plane of each crystal is parallel to a (10.4) plane of the other and that the two crystals have a closest packed direction in common, there are two possible mutual orientations. The one orientation places the principal or trigonal axes of the two crystals at 4° to one another and the other orientation makes this interaxial angle 52°. The experimental conditions under which each phase gave rise to the oscillating crystal pattern, previously discussed, indicates that the former orientation is alone possible.

A stereographic projection of a single matrix crystal with its six hypothetical orientations of segregate is shown in Fig. 14.

Mechanism of Segregation

A mechanism for the separation of the ϵ phase can be readily hypothesized on the basis of the suggested crystallographic solution of the segregate structure. The ϵ phase has a higher copper content than the η phase and the differences in interatomic distances shown in Fig. 13 are fundamentally due to the different space requirements or atomic sizes of copper and zinc. When, owing to the migration of atoms within an η crystal, the concentration of copper atoms becomes high at one point, the atoms will assume or tend to assume the atomic arrangement in ϵ. If the conditions of concentration and temperature are suitable, this very small aggregate of atoms disposed on the ϵ arrangement will remain stable and may serve as a nucleus for further segregation at that point. The influence of the orientation of the parent crystal on that of the segregate is readily seen. No complicated atomic movements are required to go from one lattice to the other, the only requirement being a high enough temperature to allow atoms to migrate within their own lattice to produce momentarily high concentrations of copper atoms.

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[15] The selection of the (10.4) plane of ϵ as the plane of separation in common with the (10.4) plane as η is the only one that is in agreement with the theory of R. F. Mehl and with the generalization of C. H. Mathewson and D. W. Smith. The former requires a similarity of the conjugate planes in atomic arrangement and interatomic distances and the latter requires each of the two planes to contain the closest packed directions of atoms of the two lattices. Atomic planes in ϵ which have atomic packing density within 20 per cent of that of the (10.4) plane of η are (12.1), (12.0), (20.3), (10.4), (20.1), (11.2) and (10.3). In only three cases, (12.0), (10.4) and (11.2), does a rectangular arrangement of atoms exist (as in (10.4) of η), and of these three only the (10.4) is even approximately similar in dimensions to the (10.4) plane of η. Furthermore, among these three planes only the (10.4) plane contains the closest packed string of atoms.

SUMMARY

The segregate structures that may be formed when the ϵ phase precipitates from the η solid solution of copper in zinc have been studied crystallographically.

The segregate forms as distinct plates parallel to matrix planes of the form {10.4}.

From theoretical and experimental considerations the orientation of the segregate relative to the matrix has been hypothesized. The suggested orientation is such that: (1) a (10.4) plane of the segregate is parallel to a (10.4) plane of the solid solution matrix; (2) the closest packed directions in the two planes, which are at the same time directions of closest possible atomic packing in this type of lattice, are coincident; and (3) the principal axes of the segregate crystals are at 4° to the principal axis of the parent matrix crystal.

A mechanism for the segregation phenomenon has been suggested.

ACKNOWLEDGMENT

The writers express appreciation to other members of the Research Division, The New Jersey Zinc Co., who gave assistance during the course of the investigation and in the preparation of the manuscript.

DISCUSSION

(*Frederic E. Carter presiding*)

W. P. DAVEY, State College, Pa.—It is a pleasure to point out that the careful work of these authors has furnished us with a most valuable confirmation of certain theories of the nature of the crystalline state. These theories go back in their origin to early work on the intensities of X-rays diffracted by crystals, and finally lead to Zwicky's formal statement of the bi-plane theory.

R. F. MEHL, Pittsburgh, Pa. (written discussion).—This competent work is a welcome addition to studies on the crystallography of the formation of segregate structures, for though segregate structures of the Widmanstätten type from hexagonal matrix lattices have been observed previously, this is the first analysis of structures formed from such lattices.

It is interesting to note that the plates of the ϵ phase do not form on the densest-packed plane of the hexagonal lattice. The analysis of lattice similarities performed by the authors fortifies much of the present theory of the formation of these structures, for theory does not predict that the plane should be the densest, but merely that it be similar to the conjugate plane in the segregate. The comparison between the {10.4} plane in the matrix, demonstrated by the authors as the plane of segregation, with the various planes in the segregate is reassuring, but I think that the theoretical aspects of the problem would be most completely served by a comparison of each of the important planes in the matrix with each of the important planes in the segregate, in order to show that of all possible cooperating planes in the two lattices the two selected fulfill the theoretical requirements most satisfactorily. This would be a tedious task, but might be fairly easily done with the help of shadows cast by lattice models, which would permit a rapid plotting of atom projections like that shown in Fig. 13.

The two possible orientations of segregate lattice upon the (10.4) plane of the matrix, discussed on page 127, are particularly interesting. The one orientation, in which the trigonal axes of the two crystals are at an angle of but 4° from one another, represents an orientation, apparently into which the matrix atoms move with a minimum amount of atom displacement. The other orientation, in which the trigonal axes are at 52°, represents an orientation bearing a twinlike relationship to the matrix lattice; a much greater atom movement or rearrangement would be necessary to produce this orientation. The authors believe that they have shown the first orientation alone to be possible. We see here, then, that the postulate of least atomic movement or rearrangement, proposed as general in the formation of Widmanstätten figures, is confirmed.

The paper by Mathewson and Smith[16] might well be considered in connection with the present work. That directions play an important part in determining the orientation of the segregate lattice cannot be doubted. Matching of directions upon conjugate planes determines the number of orientations of segregate upon a single matrix plane, as we have found for the precipitation of ferrite from austenite in hypoeutectoid steel. I am inclined to doubt, however, that the most densely packed directions determine the plane of segregation. If we accept the hypothesis that the conjugate planes are those most nearly alike in the two lattices, and if we add the postulate that the transformation will, when possible, take place by atom movement or rearrangement on simple, low index planes, since in this case the atom movement or rearrangement is relatively more simple, we may see the reason for the fact that the conjugate planes usually contain close-packed directions. Inspecting the first 22 most densely packed planes in the face-centered cubic lattice in order of decreasing density, we find that the close-packed direction [110] occurs in four of the first five planes, in one of the second five, in one of the third, and in one of the fourth; a similar inspection of 32 planes in the body-centered cubic lattice shows that the close-packed direction [111] occurs in three of the first five planes, in one of the second five, in none of the third, in one of the fourth, in none of the fifth, and in one of the sixth. As might well be expected, the close-packed direction in a lattice occurs more frequently in the more densely packed planes than in the less densely packed. Accordingly, if simple planes are chosen for segregation, the chances are good for these planes to contain the densely packed direction. If planes of higher index are chosen—which we may expect when the precipitate lattice is one of low symmetry—the chances are poor; this is the case for the precipitation of Fe_4N from the solid solution of nitrogen in α iron occurring on the {210} plane in α iron which does not contain the close-packed direction [111]. In such a case the most closely packed directions on the conjugate planes would probably prove on analysis to be parallel, though the direction in the matrix plane cannot be the most densely packed direction in the lattice and that in the precipitate plane may not be. From this point of view, closest packed directions play no primary part in the selection of conjugate planes. Their usual, though not general, occurrence in such planes is simply a corollary of their usual occurrence in planes of low index.

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[16] Reference of footnote 1.

F. N. Rhines, New Haven, Conn. (written discussion).—In footnote 14, the authors say that the X-ray reflections from particles of the precipitated phase were not recorded on the oscillating film of the Davey-Wilson camera, while they were sharply defined on the stationary film. In commenting upon this observation they appear to have said that it could be accounted for either by a lack of perfection (I presume that they mean the presence of distortion) in the crystals, or by a lack of agreement in the mutual orientations of similarly oriented plates of the segregate.

Do the authors consider that a distortion of the crystal lattices sufficient to obliterate the record on the oscillating film would at the same time be recognizable by a lack of definition in the spot on the stationary film? If so, and if no such lack of definition was noted (that is, if the spots on the stationary film resulting from the parent and segregated phases were equally well defined), the absence of the spots on the oscillating film must be due to the second cause; namely, a real spread among the orientations of the lattices of the individual particles of the precipitate.

Such a conclusion is in agreement with the spread in the directions of the traces of the precipitated plates recorded in Figs. 5 to 8 inclusive. In these plots the measured directions seem to vary at least as much as ±5° from the mean value, giving a total spread of 10° for each group of plates. This would be ample to account for the obliteration of the X-ray spots on the oscillating film, since it would spread the radiation over an arc of about 20° on the film.

This observation, if correct, lends weight to the suggestion, previously made by Dr. Mehl, that the orientation of the precipitating phase is determined by the registry of its atoms with those of the parent crystal in the very early stages of the precipitation *only*. Thus the existence of a considerable spread in the orientation of the segregated particles seems to indicate an independence of their structure from that of the parent crystal during the greater part of their growth. A spread in the orientations of the original nuclei of the precipitate is easily understood, because they would be influenced by localized irregularities in the lattice of the parent crystal, which could probably have a much greater angular magnitude than could distortions of the crystal as a whole. Incidentally, such a condition is required by the theory of "pre-precipitation hardening."

AMERICAN INSTITUTE OF MINING AND METALLURGICAL ENGINEERS
Contribution No. 11 (CLASS E, INSTITUTE OF METALS DIVISION), FEBRUARY, 1933

DISCUSSION OF THIS PAPER IS INVITED. It should preferably be presented at the New York Meeting, February, 1933, when an abstract of the paper will be read. If this is impossible, discussion in writing may be sent to the Editor, American Institute of Mining and Metallurgical Engineers, 29 West 39th Street, New York, N. Y., for presentation by the Secretary or other representative of its author. Unless special arrangement is made, the discussion of this paper will close April 1, 1933. Any discussion offered thereafter should preferably be in the form of a new paper.

Rate of Precipitation of Nickel Silicide and Cobalt Silicide in the Hardenable Copper-nickel-silicon and Copper-cobalt-silicon Alloys

BY CURTIS L. WILSON,* BUTTE, MONT., HORACE F. SILLIMAN,† WATERBURY, CONN., AND EUGENE C. LITTLE,‡ BUTTE, MONT.

(New York Meeting, February, 1933)

FROM the results of his investigation of the hardenable copper-nickel-silicon and copper-cobalt-silicon alloys, M. G. Corson[1] explained the dispersion-hardening effect by assuming the precipitation of the intermetallic compounds nickel silicide and cobalt silicide, and on this basis he constructed diagrams for the pseudobinary systems copper-nickel silicide and copper-cobalt silicide.

A consideration of these diagrams and of the factors that exert such an important influence upon the rate of precipitation, such as degree of supersaturation, nucleus number and rate of diffusion, leads to the expectation that the rate of precipitation of the silicides on reheating the quenched solid solutions at temperatures below the alpha-phase boundary should increase continuously as the reheating temperature is raised. The present investigation shows that while this rate does increase with the reheating temperature in a general way, it does not do so continuously. Supplements to Corson's diagrams are offered, showing the discontinuities, and slight modifications in the solubility curves are suggested.

EXPERIMENTAL PROCEDURE

Alloys were prepared by melting together the required amounts of electrolytic copper,[2] silicon,[3] shot nickel[4] and cobalt,[5] in covered graphite crucibles in a carbon resistance furnace, the copper being brought first into the liquid condition and the silicon and nickel or cobalt added in the proportions to produce Ni_2Si or Co_2Si. Chemical analyses were

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* Professor of Metallurgy, Montana School of Mines.

† Assistant Metallurgist, American Brass Co.

‡ Research Fellow in Metallurgy, Montana School of Mines.

[1] *Proc.* Inst. Met. Div., A.I.M.E. (1927) 435–450. *Rev. de Mét.* (1930) **27,** 83–101, 133–153, 194–213, 265–281.

[2] From Anaconda Copper Mining Co.

[3] From Electrometallurgical Sales Corp.

[4] From International Nickel Co.

[5] From Central Scientific Co.

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made on all alloys to confirm these proportions. The molten metal was held at 1350° C. for 40 min., cooled to 1200° C., cast into molds machined from blocks of graphite, and chilled as soon as solidified. The cast billets were hammered and either passed through a set of hand rolls or drawn into wire through steel dies.

The heat treatment of both sheet and wire consisted of quenching the alloys from a temperature within the homogeneous alpha field and then reheating for various lengths of time at temperatures below the solubility boundary. Microscopic examinations were made to ascertain that the specimens had been held long enough at the quenching temperature to insure complete solubility of the silicides. A slightly reducing atmosphere was maintained so that all quenched and annealed specimens were bright and clean.

Hardness tests were made on the Rockwell machine type 2½ H, using the B scale, 1/16-in. ball, 100-kg. load, following the technique proposed by Townsend, Straw and Davis.[6] The resistance measurements on the nickel silicide alloy were made at 20° C. with a Wheatstone bridge. On the cobalt silicide alloys the measurements were made in the furnace at the temperature of annealing by means of a Leeds & Northrup type K potentiometer, the resistance being calculated from the IR drop and the milliammeter reading. Inasmuch as the rate of precipitation as indicated by the change in resistance was the phenomenon upon which evidence was sought, all resistances were measured or calculated in ohms arbitrarily for the wire being tested, without any attempt at determining specific resistances.

Precipitation of Nickel Silicide

The solid solution obtained by quenching the nickel silicide alloys from temperatures in the alpha field has, of course, a rather high electrical resistance. Reheating at temperatures below the alpha-phase boundary brings about the precipitation of nickel silicide and the resistance is thereby decreased. The rate at which the precipitation takes place is indicated by the resistance measurements shown graphically in Figs. 1 and 2, which show that the rate of decrease of the electrical resistance becomes greater as the reheating temperature rises, up to a certain point. This point is around 500° C. for the 2 per cent Ni_2Si alloy and around 600° C. for the 5 per cent alloy. Above these temperatures a decrease in the rate of precipitation appears. As shown in Fig. 1, the slope of the 550° curve during the first few hours is not as steep as that of the 500° curve; in other words, the rate of precipitation of the Ni_2Si from solution is less at a reheating temperature of 550° C. than it is at a reheating temperature of 500° C. Similarly in Fig. 2, the slope of the 750° curve is less than that of the 600° curve, indicating a similar decrease in the rate of precipitation at the higher of the two reheating temperatures.

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[6] Amer. Soc. Test. Mat. *Preprint* 46 (1929).

Were the decreased rate of precipitation at higher temperatures due entirely to a lesser degree of supersaturation, in Fig. 1 the rate at 650° C. would be less than at 550° C. The fact that the 650° curve has a steeper slope than the one for 550° suggests the possibility of another transformation in Corson's $\alpha + Ni_2Si$ field.

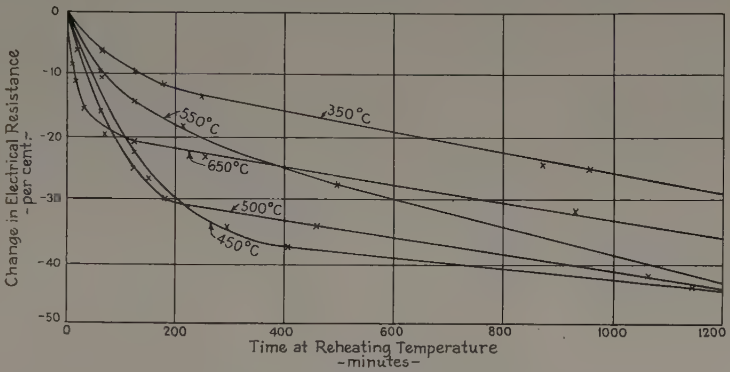

FIG. 1.—CHANGE IN ELECTRICAL RESISTANCE ON REHEATING COPPER + 2 PER CENT Ni_2Si. QUENCHED FROM 700° C. REHEATED AT TEMPERATURES INDICATED.

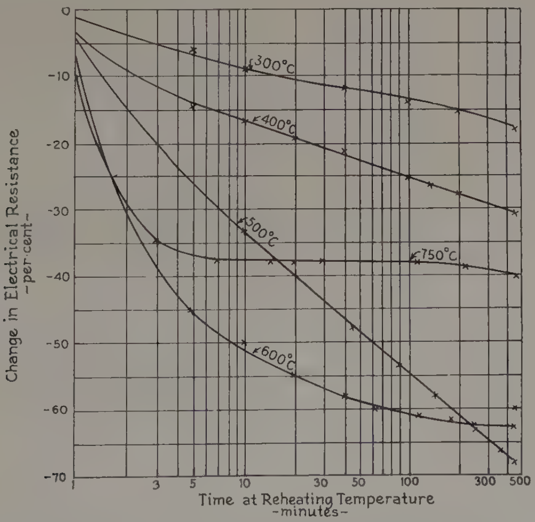

FIG. 2.—CHANGE IN ELECTRICAL RESISTANCE ON REHEATING COPPER + 5 PER CENT Ni_2Si. QUENCHED FROM 900° C. REHEATED AT TEMPERATURES INDICATED.

Therefore specimens were reheated at a number of temperatures below the alpha-phase boundary and two temperature limits found for each of a series of alloys of various compositions, between which limits the electrical resistance changed markedly. This difference in resistance amounted to as much as 15 per cent, and could be noted easily, regardless of whether

TABLE 1.—*Variations in Resistance*

Heat Treatment	Resistance, Ohm	Change in Resistance	
		Ohm	Per Cent
1. COPPER + 2 PER CENT Ni_2Si			
Quenched from 700°	0.197		
Heated at 350° to 450° for 40 hr	0.136	−0.061	−31.0
Raised to 600° for 30 min	0.148	+0.012	+ 8.1
Heated at 500° for 30 min	0.119	−0.024	−16.3
Heated at 550° for 30 min	0.131	+0.012	+10.1
Heated at 525° for 15 min	0.121	−0.010	− 7.6
2. COPPER + 3 PER CENT Ni_2Si			
Quenched from 800°	0.237		
Heated at 500° for 12 hr	0.119	−0.118	−49.6
Heated at 600° for 30 min	0.140	+0.021	+17.8
Heated at 550° for 30 min	0.132	−0.008	− 5.7
Heated at 565° for 30 min	0.127	−0.005	− 3.8
Heated at 585° for 30 min	0.131	+0.004	+ 3.1
3. COPPER + 4 PER CENT Ni_2Si			
Quenched from 850°	0.298		
Heated at 525° for 12 hr	0.160	−0.138	−46.3
Heated at 685° for 30 min	0.194	+0.034	+17.5
Heated at 625° for 30 min	0.164	−0.030	−15.5
Heated at 650° for 30 min	0.176	+0.010	+ 5.7
4. COPPER + 5 PER CENT Ni_2Si			
Quenched from 900°	0.358		
Heated at 525° for 12 hr	0.173	−0.185	−51.7
Heated at 650° for 30 min	0.174	+0.001	00.0
Heated at 700° for 30 min	0.200	+0.026	+15.0
Heated at 675° for 30 min	0.183	−0.017	− 8.8
5. COPPER + 6 PER CENT Ni_2Si			
Quenched from 900°	0.391		
Heated at 650° for 10 hr	0.223	−0.168	−43.0
Heated at 700° for 25 min	0.255	+0.032	+14.9
Heated at 640° for 45 min	0.224	−0.031	−13.9
Heated at 675° for 30 min	0.238	+0.014	+ 5.8
6. COPPER + 7 PER CENT Ni_2Si			
Quenched from 975°	0.441		
Heated at 450° for 8 hr	0.177	−0.234	−53.0
Heated at 650° for 30 min	0.184	+0.007	+ 4.0
Heated at 625° for 30 min	0.166	−0.018	−10.8
Heated at 700° for 15 min	0.206	+0.040	+24.1
7. COPPER + 8 PER CENT Ni_2Si			
Quenched from 1000°	0.398		
Heated at 475° for 18 hr	0.162	−0.236	−53.0
Heated at 550° for 30 min	0.160	−0.002	− 1.8
Heated at 625° for 15 min	0.186	+0.026	+14.0
Heated at 575° for 15 min	0.160	−0.026	−14.0
8. COPPER + 9 PER CENT Ni_2Si			
Quenched from 1025°	0.440		
Heated at 425° for 18 hr	0.144	−0.296	−67.0
Heated at 525° for 30 min	0.142	−0.002	− 1.5
Heated at 575° for 15 min	0.158	+0.016	+10.0
Heated at 540° for 30 min	0.158	0.000	0.0
Heated at 525° for 10 min	0.151	−0.007	− 4.6

the specimens were heated from the lower to the higher temperature or cooled from the higher to the lower. Inasmuch as the resistances were so delicately dependent upon temperature, decreasing with increased reheating temperature and increasing with decreased temperature, it was assumed that real equilibrium had been attained. Furthermore, as the rates of change were so obviously abrupt within the temperature limits determined, the differences were not ascribed to alternate precipitation and solution of nickel silicide.

Table 1 gives examples, which were reproducible, of how the resistances varied back and forth. In Fig. 3 the values tabulated in the tables are plotted in the $\alpha + Ni_2Si$ field of Corson's diagram, and a curve is drawn to separate the phase of distinctly higher resistance from that of lower resistance. Over a period of months, no appreciable precipitation of Ni_2Si, as indicated by a change in electrical resistance, took place at room temperatures.

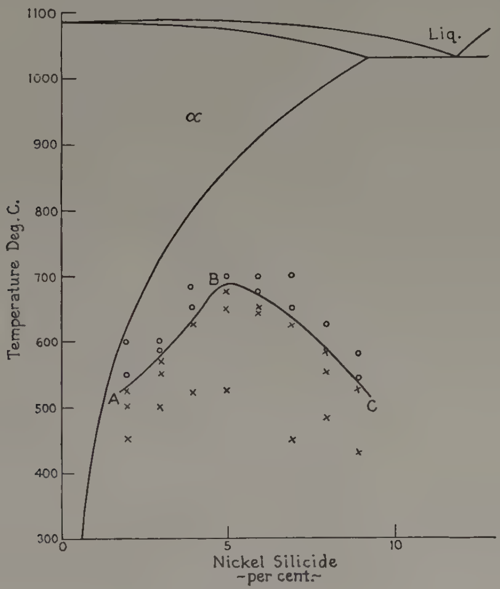

FIG. 3.—SYSTEM COPPER-NICKEL SILICIDE AS MODIFIED.

The discontinuities in the rate of precipitation as recorded by the resistance measurements were studied by means of microscopic examinations, using Vilella's reagent[7] as an etchant. The specimens shown in Figs. 4, 7, 10 and 13 were quenched from the homogeneous alpha field. The alloy with 8 per cent Ni_2Si (Fig. 13) contained more of the compound than could be driven into solution under the conditions maintained. Figs. 5, 8, 11 and 14 represent the specimens that were reheated, following

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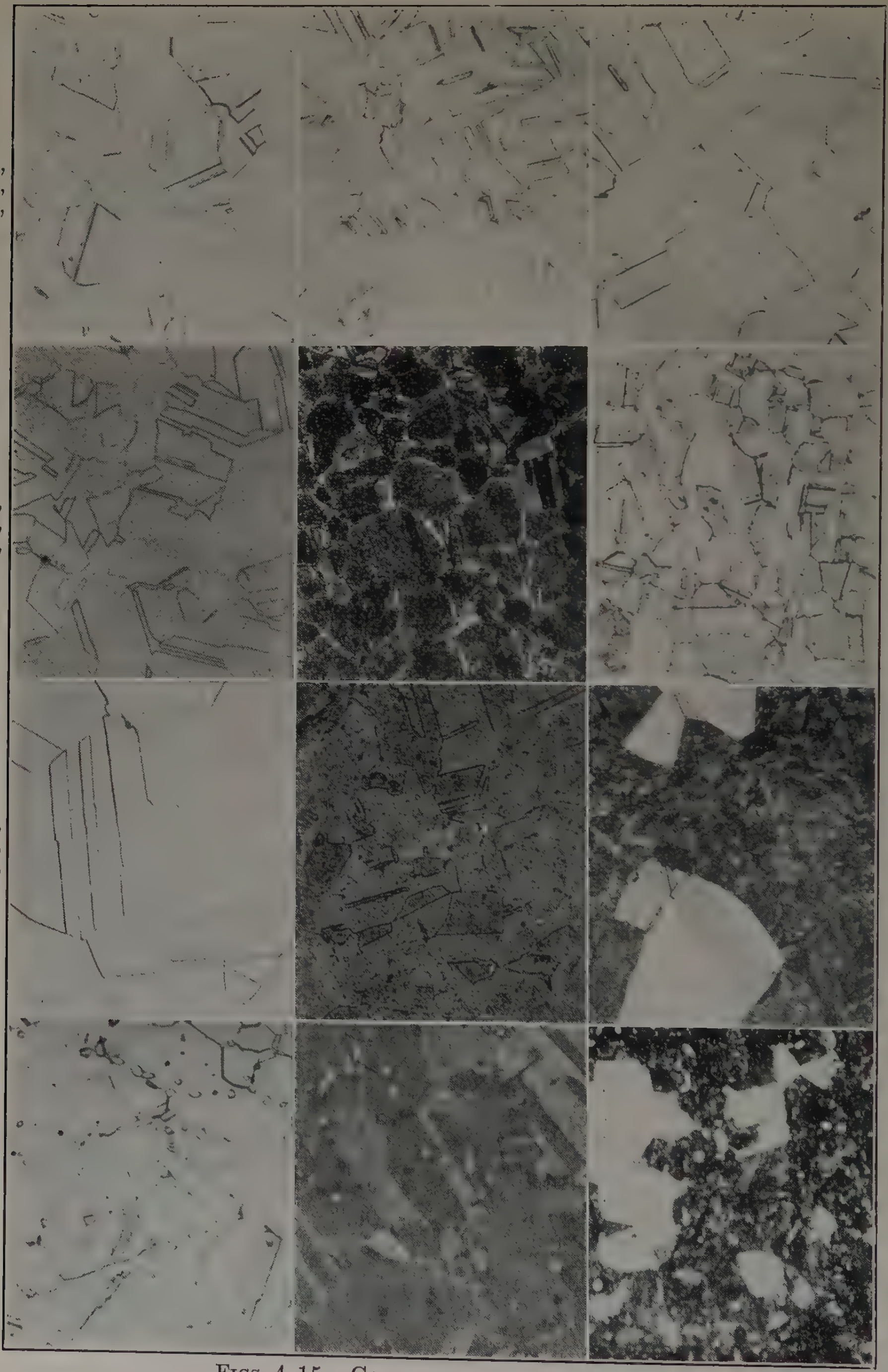
[7] Sat. $K_2Cr_2O_7$ solution plus HCl.



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FIGS. 4–15.—CAPTIONS ON OPPOSITE PAGE.
Read left to right on each line for order of figure numbers.

quenching, to a temperature below the alpha-phase boundary but above the line *ABC* in Fig. 3. The precipitation of Ni_2Si is evident in Figs. 8, 11 and 14, but not so evident in Fig. 5, owing probably to the small amount of the compound present or to the submicroscopic dispersion. Figs. 6, 9, 12 and 15 show specimens that were reheated to temperatures below the line *ABC* in Fig. 3. The structure of these alloys differs sharply from that of the alloys reheated at a somewhat higher temperature, and it is believed that another transformation takes place along the line *ABC* of Fig. 3. This transformation may be an allotropic one or a change in the solubility forming a new eutectoidal constituent.

The hardness of the heat-treated alloys was found to depend upon the percentage of nickel silicide present, the quenching temperature, the temperature of reheating the quenched specimens, and the length of time during which the specimens were held at the reheating temperature. The change of hardness with time of reheating is shown for the 2 and 5 per cent alloys in Figs. 16 and 17. These curves confirm those obtained by resistance measurements to the effect that the higher the reheating temperature, the more rapid is the rate of precipitation of nickel silicide. A discontinuity in the increase in rate of precipitation is noted between 600° C. and 650° C. for the 5 per cent alloy. The decrease in hardness after certain maxima have been reached will be recognized as due to coagulation.

It is known that the Rockwell hardness of copper alloys is more or less inversely proportional to the grain size, and that the grain size in turn is a function of the temperature from which the alloy is quenched. This was found to be true for the copper-nickel-silicon alloys investi-

TABLE 9.—*Effect of Quenching Temperature on Hardness*

Copper + 2 per cent Ni_2Si quenched from various temperatures after 70 per cent reduction by cold rolling

QUENCHING TEMP., DEG. C.	ROCKWELL HARDNESS, 60 KG.
700	67
800	57
900	53.5
1000	51

FIGS. 4–6.—COPPER + 2 PER CENT Ni_2Si. QUENCHED FROM 900° C. × 200.
FIG. 5 REHEATED AT 600° C.
FIG. 6 REHEATED AT 500° C.

FIGS. 7–9.—COPPER + 4 PER CENT Ni_2Si. QUENCHED FROM 900° C. × 200.
FIG. 8 REHEATED AT 750° C.
FIG. 9 REHEATED AT 500° C.

FIGS. 10–12.—COPPER + 6 PER CENT Ni_2Si. QUENCHED FROM 1000° C. × 200.
FIG. 11 REHEATED AT 750° C.
FIG. 12 REHEATED AT 500° C.

FIGS. 13–15.—COPPER + 8 PER CENT Ni_2Si. QUENCHED FROM 1000° C. × 200.
FIG. 14 REHEATED AT 750° C.
FIG. 15 REHEATED AT 500° C.

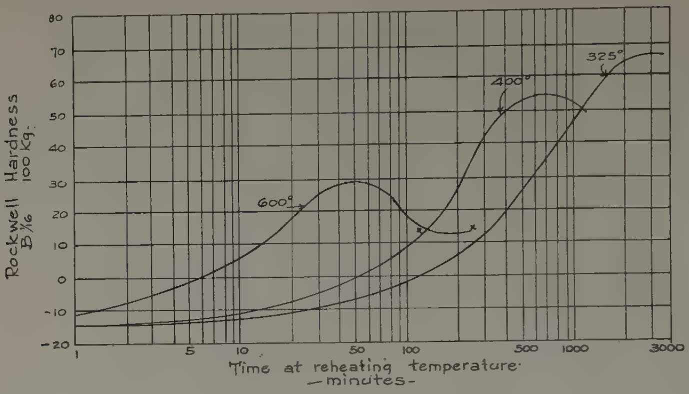

FIG. 16.—CHANGE IN HARDNESS ON REHEATING COPPER + 2 PER CENT Ni_2Si. QUENCHED FROM 900° C. REHEATED AT TEMPERATURES INDICATED.

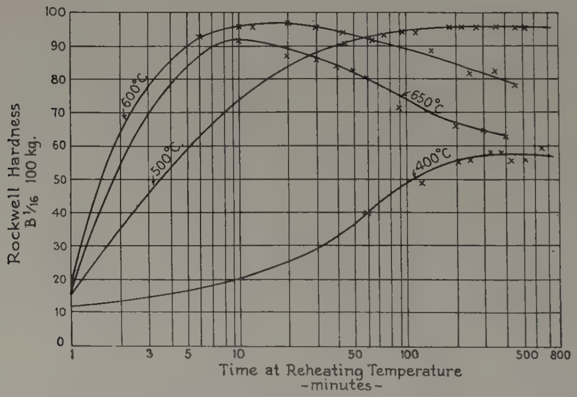

FIG. 17.—CHANGE IN HARDNESS ON REHEATING COPPER + 5 PER CENT Ni_2Si. QUENCHED FROM 900° C. REHEATED AT TEMPERATURES INDICATED.

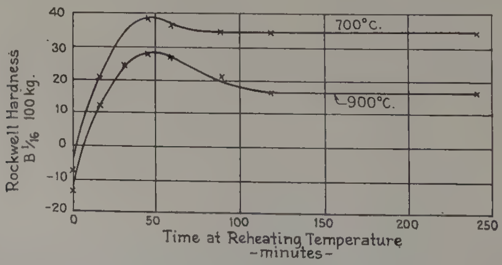

FIG. 18.—EFFECT OF QUENCHING TEMPERATURE ON HARDNESS; COPPER + 2 PER CENT Ni_2Si. QUENCHED FROM TEMPERATURES INDICATED. REHEATED AT 600° C.

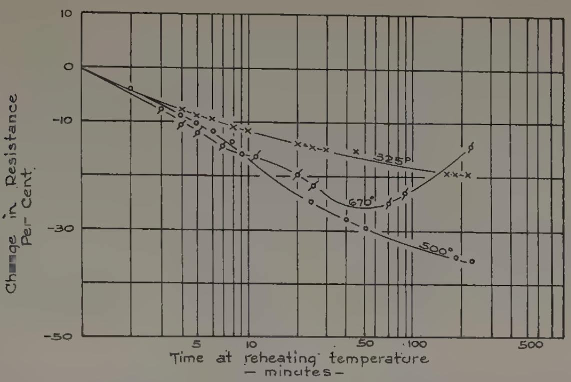

FIG. 19.—CHANGE IN ELECTRICAL RESISTANCE ON REHEATING COPPER + 2 PER CENT Co_2Si. QUENCHED FROM 970° C. REHEATED AT TEMPERATURES INDICATED.

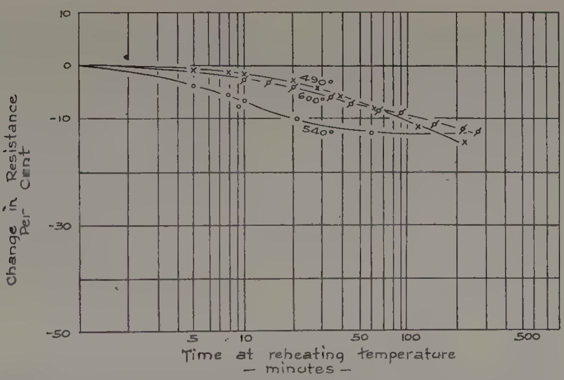

FIG. 20.—CHANGE IN ELECTRICAL RESISTANCE ON REHEATING COPPER + 4 PER CENT Co_2Si. QUENCHED FROM 970° C. REHEATED AT TEMPERATURES INDICATED.

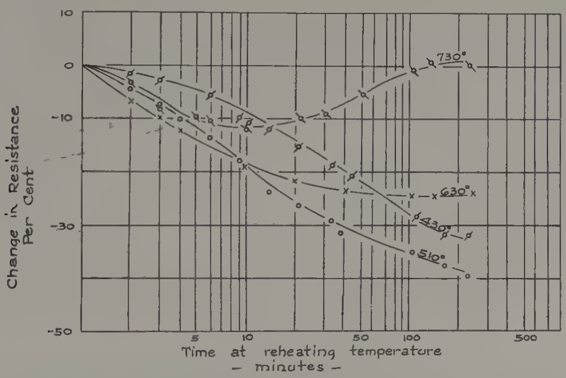

FIG. 21.—CHANGE IN ELECTRICAL RESISTANCE ON REHEATING COPPER + 5 PER CENT Co_2Si. QUENCHED FROM 970° C. REHEATED AT TEMPERATURES INDICATED.

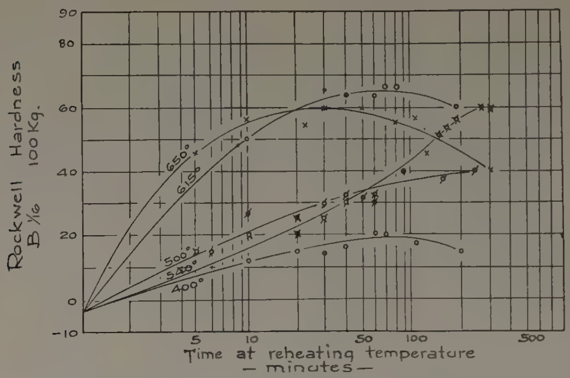

FIG. 22.—CHANGE IN HARDNESS ON REHEATING COPPER + 2 PER CENT Co_2Si. QUENCHED FROM 930° C. REHEATED AT TEMPERATURES INDICATED.

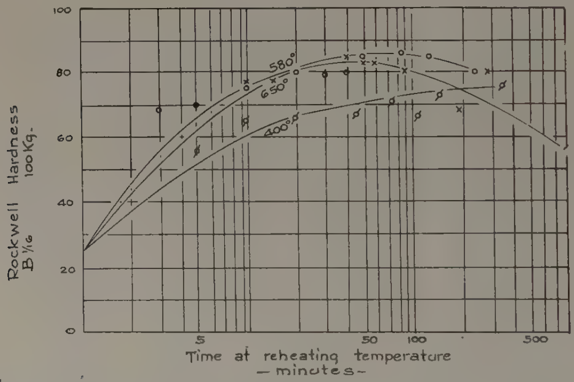

FIG. 23.—CHANGE IN HARDNESS ON REHEATING COPPER + 4 PER CENT Co_2Si. QUENCHED FROM 970° C. REHEATED AT TEMPERATURES INDICATED.

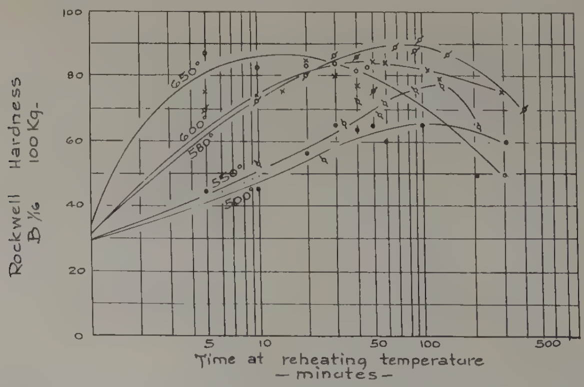

FIG. 24.—CHANGE IN HARDNESS ON REHEATING COPPER + 5 PER CENT Co_2Si. QUENCHED FROM 970° C. REHEATED AT TEMPERATURES INDICATED.

gated here, as shown in Table 9, where the hardness decreased with rising temperature. The time of annealing and the quenching temperature were such that all of the nickel silicide was in solid solution.

That the quenching temperature has a decided influence upon the precipitation hardness obtainable by reheating the quenched specimens is shown likewise by Fig. 18. The maximum hardness evidently can be attained by quenching from just above the alpha-phase boundary. Fig. 18 indicates that the quenching temperature seemed to have no effect upon the rate of precipitation, for the maximum hardness was attained after the same reheating time for both quenching temperatures.

Precipitation of Cobalt Silicide

The rate of precipitation of cobalt silicide from the quenched solid solutions, as measured by the change in electrical resistance, is shown in Figs. 19 to 21. The increase in resistance after a decrease to a minimum, as noted in Fig. 19 at a reheating temperature of 670° C. and in Fig. 21 at 730° C., is attributed to grain growth.[8]

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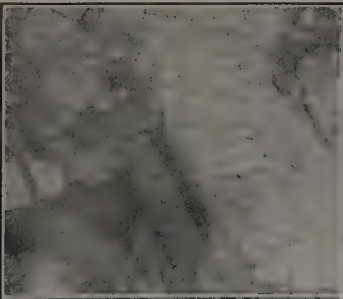

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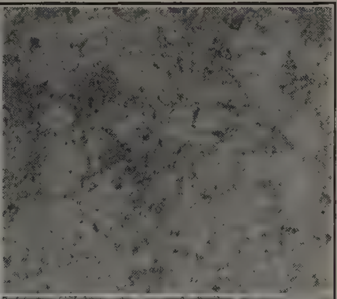

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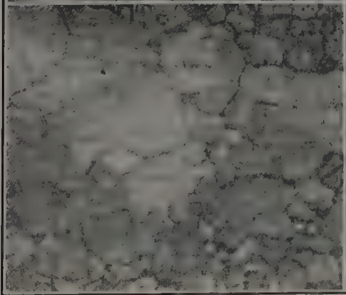

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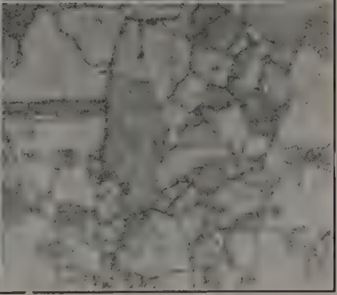

Fig. 25.—Copper + 4 per cent Co_2Si. Quenched from 980° C. × 300.
Fig. 26.—Copper + 4 per cent Co_2Si. Quenched from 910° C. × 300.
Fig. 27.—Copper + 5 per cent Co_2Si. Quenched from 980° C. × 300.
Fig. 28.—Copper + 5 per cent Co_2Si. Quenched from 910° C. × 300.

Had the rate of precipitation increased continuously with increasing reheating temperature, the slopes of the curves would have increased continuously for each increased temperature. Discontinuities in the slope, and therefore in the rate of precipitation, occur after 10 min. between 500° and 670° C. for the 2 per cent Co_2Si alloy, between 540° and 600° C. for the 4 per cent alloy, and between 510° and 630° C. for the 5 per cent alloy.

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[8] Credner: *Ztsch. f. physik. Chem.* (1913) **82**, 457.

The change in hardness as an indication of the rate of precipitation is shown in Figs. 22 to 24. Discontinuities occur in these curves between 500° and 540° C. for the 2 per cent alloy and between 580° and 650° C. for the 4 per cent alloy.

SOLUBILITY OF COBALT SILICIDE

Microscopic examination of the cobalt silicide alloys containing 4 and 5 per cent Co_2Si, which had been quenched from 980° C., showed a homogeneous solid solution, even at magnifications as high as 2600 dia. Quenching from 910° C., however, produced specimens in which the particles of Co_2Si were visible. From the photomicrographs in Figs. 25 to 28, the solubility curve of Fig. 29 is suggested.

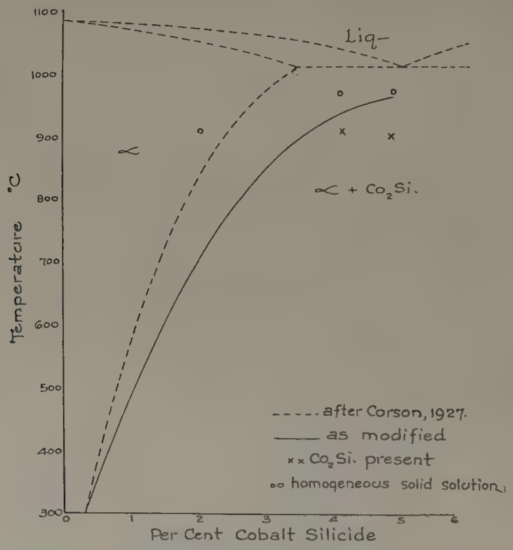

FIG. 29.—SYSTEM COPPER-COBALT SILICIDE.

The Rate of Precipitation of Nickel Silicide and Cobalt Silicide in the Hardenable Copper-nickel-silicon and Copper-cobalt-silicon Alloys*

By Curtis L. Wilson,† Butte, Mont., Horace F. Silliman,‡ Waterbury, Conn., and Eugene C. Little,§ Butte, Montana

(New York Meeting, February, 1933)

Abstract

The change in electrical resistance and Rockwell hardness (16-100-B) of copper alloys containing Ni_2Si and Co_2Si was determined by annealing the quenched solid solutions at various temperatures for various lengths of time. The rate of precipitation of Ni_2Si, as measured by the rate of decrease of electrical resistance and increase of hardness, increased with annealing temperature up to a certain point, depending on the percentage of Ni_2Si present. At these temperatures discontinuities in the rates of change occurred. Similar discontinuities in the Co_2Si alloys were noted. The solubility of Co_2Si in copper was found to be 5 per cent at 970° C.

DISCUSSION

(Robert F. Mehl presiding)

R. F. Mehl, Pittsburgh, Pa. (written discussion).—The electrical conductivity and hardness curves reported in this paper are interesting, particularly because many of the anomalies of the precipitation processes are evident from such curves. The title of the paper, however, is deceptive, for it implies that measurements of electrical conductivity and hardness are suitable to determine the rate of precipitation. Neither of these methods is suitable for a quantitative measurement of rates of reaction or of precipitation in the solid state. Electrical conductivity in some alloys shows an anomalous increase during the first stages of aging at low temperatures; it is notably sensitive to strain and to state of subdivision. I have plotted the conductivity curve representing the decomposition of the β phase at 555° C. in the copper-aluminum system, given in the paper by Smith and Lindlief (Fig. 47, p. 93) as a rate of reaction curve, and compared it with the curve determined by area evaluation (Fig. 7); these two curves are not coincident. Hardness is likewise very uncertain, for it is so much dependent upon particle size.

Of the various methods proposed for the study of rates of reaction and precipitation, the evaluation of volume of reaction product from the respective area of matrix and reaction product on the photomicrograph is the most trustworthy; suffering, perhaps, only from low sensitivity during the early stages. This method, used originally by Davenport and Bain and now by Smith and Lindlief, is suitable for eutectoid transformations, but is of little use for precipitation from solid solutions of the type studied by Wilson, Silliman and Little, because the microscope is deceptive when used to evaluate areas in systems of this sort. The area method has the further distinct advantage of being an absolute method, not a difference method. The dilatometric method, though a difference method, in general is satisfactory. Its usefulness depends, of course, on the difference in volume in the system before and after transformation, and when this difference is small the method loses sensitivity. For some alloys, particularly austenitic alloy steels, certain magnetic properties may be used in evaluating the extent of transformation, as Wever recently has done for chromium steels. In this case it seems fairly certain that the property measured is directly proportional to the amount of the ferromagnetic ferrite formed. Next in order of trustworthiness come electrical conductivity and hardness. In both these cases the interpretation of changes in properties into degree of transformation or precipitation depends on the assumption of some functional relation between the property measured and the degree of transformation; this functional relationship is in general unknown. When measurements of electrical conductivity and hardness are made, it is better merely to state that such measurements have been made during the progress of the transformation or precipitation process without implying a knowledge of the undetermined functional relationship of these properties with the degree of transformation or precipitation.

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* This paper is available at the office of the Institute as *Contribution No.* 11.

† Professor of Metallurgy, Montana School of Mines.

‡ Assistant Metallurgist, American Brass Co.

§ Research Fellow in Metallurgy, Montana School of Mines.

The objections I have raised are not so serious when the measurements are made at high temperatures, since the observed anomalies in these properties are not so pronounced then, but in the absence of a demonstration of the functional relationship the use of these properties to determine rates of precipitation is unjustified.

C. S. Sivil, Newark, N. J. (written discussion).—The authors have brought out one or two interesting points in the age-hardening of the copper-nickel silicide alloys. The variations in rate of precipitation in Figs. 1 and 2 are of great interest and show that the mechanism of the reactions is not as simple as that suggested by Corson.[1]

However, I feel that the paper is not complete. There is a portion that needs to be amplified considerably. The statement is made that "the quenching temperature has a decided influence on the precipitation-hardness obtainable by reheating the quenched specimens." In support of this statement two curves are presented in Fig. 18, which show a variation of age-hardening in specimens of an alloy of copper with 2 per cent Ni_2Si quenched from 700° C. and 900° C., and both reheated at 600° C. Now, Fig. 16 shows that in the case of the 900° C. quench, 600° C. is not the optimum reheating temperature but is actually the most unfavorable temperature of the three reported. No curves are included showing the effect of reheating at various temperatures of specimens quenched from 700° C. To support a statement of the nature of that quoted above, such curves should be presented and the reheating temperature should be comparable in each series; that is, the optimum reheating temperature should be chosen for each quenching temperature.

If dispersion hardening is considered to be the true mechanism of age-hardening there seems to be no reason why the quenching temperature should affect the maximum hardness obtainable on aging, unless the hardness after aging is the sum of the hardness due to grain size and that due to the precipitation of Ni_2Si. Unfortunately the results of the hardness after quenching from various temperatures are given with a 60-kg. load while the hardness due to tempering is found with a 100-kg. load. I know of no method of correlating these data. It seems possible that the effect of quenching temperature on the hardness obtainable by aging may be more upon the optimum temperature of aging than upon the maximum hardness obtainable by aging.

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[1] M. G. Corson: *Proc.* Inst. Met. Div., A.I.M.E. (1927) 435–450; *Rev. de Mét.* (1930) **27**, 83–101, 133–153, 194–213, 265–281.

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The Solubility of Gases in Metals*

BY V. H. GOTTSCHALK† AND R. S. DEAN,‡ WASHINGTON, D. C.

(New York Meeting, February, 1932)

THE solubility of gases in metals has been of interest since Graham's time in 1866, but, although the subject was actively studied by iron and steel metallurgists during the eighties, the era of painstaking laboratory investigation begins in 1907 with the publication of Sieverts'[1] thesis on the occlusion and diffusion of gases in metals. Since then, Sieverts has worked almost continuously in this field, and his views on the subject are the prevailing ones at the present time.[2]

Probably the most important result obtained by Sieverts, and frequently verified since by other observers, is the discovery that at a constant temperature the solubility of almost all gases in both the liquid and solid state of most of the metals is proportional to the square root of the pressure (for pressure above 100 mm.). The obvious explanation of this fact is that the gas dissolves as atoms and not as molecules, although it has been pointed out a number of times, first by Donnan and Shaw[3] in connection with their work on the solubility of oxygen in silver at 1075° C., that the formation and solution of a compound of the metal and gas would also be indicated by a variation of the solubility with the square or higher root of the pressure. Sieverts[4] himself raised the question whether the usual explanation (*i. e.*, that the gas dissolves as atoms) may not be wrong, when he found that the square root law held also for the solubility of sulfur dioxide in molten copper; in which case dissociation into simpler molecules or atoms does not take place. Stubbs[5] subsequently showed that Sieverts and Krumbhaar's "constant" for sulfur dioxide dissolving in copper agreed better with the assumption of a variation of the solubility with the 2.4th root of the pressure, and gave an explanation based on measurements of the depression of the freezing point. Stubbs summarizes his results thus:

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* Published by permission of the Director, U. S. Bureau of Mines.

† Senior Physicist, Metallurgical Division, U. S. Bureau of Mines.

‡ Chief Engineer, Metallurgical Division, U. S. Bureau of Mines.

[1] A. Sieverts and P. Beckmann: Zur Kenntniss der Okklusion und Diffusion der Gase durch Metallen. *Ztsch. f. phys. Chem.* (1907) **60,** 165.

[2] Thus, Landolt-Börnstein's *Physikalisch-Chemische Tabellen*, Ed. 5, **2,** 495–498, 1931, for the first time includes data on the Absorption and Adsorption of Gases by Metals, selected from a tabulation given by Sieverts: *Ztsch. f. Metallkunde* (1929) **21,** 37.

[3] Donnan and Shaw: *Jnl.* Soc. Chem. Ind. (1910) **29,** 987.

[4] Sieverts and Krumbhaar: *Ztsch. f. phys. Chem.* (1910) **74,** 277.

[5] C. M. Stubbs: The Action of Sulphur Dioxide on Copper at High Temperature. *Jnl.* Chem. Soc. (1913) **103,** 1445–1461.

> The depression of the freezing point of copper by dissolving sulphur dioxide was found to be about 2.54 times that expected if the molecules of the gas existed unchanged in the solution. This was shown to be explicable on the hypothesis of a partial reaction of the sulphur dioxide with the copper. Complete reaction would give three times the depression calculated from the formula SO_2, and the amount of gas dissolved should vary as the cube root of the pressure.

The method of Stubbs is important, but should be studied further, chiefly as regards the applicability of van't Hoff's formula for freezing point depression to molten copper as a solvent.

In other words, the interpretation of Sieverts' square-root law and especially its application to compound gases needs further study. This much is clear, however;—the solubility of gases in metals at high temperature is a different phenomenon from the solubility of gases in water or in other liquid solvents at ordinary temperatures. This being the case, it follows that caution should be used in applying to metallurgical reactions involving gases, the quantitative relations that have been deduced and proved only for ordinary cases of solubility.

It is the object of this paper to draw attention to the need for a quantitative theory of the behavior of gases in contact with metals at high temperatures. As a preliminary to the experimental work on which such a theory must be based, discussion of recent literature of the solubility of gases in metals may be of interest. This paper presents:

1. A computation of the so-called "ideal solubility" of a gas in a hypothetical solvent having the characteristics of molten metal. This computation can be made only approximately, but the results may be taken as somewhat more definite than the usual statement made by physical chemists conversant with solubility relations, that molten metals should be very poor solvents for the ordinary gases.

2. A critical comment on recent work on the absorption of gases by hot metals. Much of this work deals with solid metals at temperatures not much below the melting point, and has been included because there seem to be reasons for believing that the processes of gas absorption just above and below the melting point do not differ much, if at all. The comments are directed towards indicating points of departure for further study.

3. An attempt to show that, in the absence of a precise theory, observed metallurgical phenomena connected with the absorption and evolution of gas may be studied advantageously, at least qualitatively, on the simple assumption that there is some sort of chemical reaction between the metal and the gas.

AN ESTIMATE OF THE SIMPLE SOLUBILITY OF GASES IN MOLTEN METALS

In what follows, the term "simple solubility" is used to mean what was formerly called "physical solubility," such as occurs when hydrogen, oxygen, nitrogen, carbon monoxide or the noble (inert) gases (He, Ar, Ne, Kr and X) dissolve in water at ordinary temperatures. The term "simple solubility" is used to exclude "chemical solubility," such as occurs when ammonia, sulfur dioxide or carbon dioxide dissolve in water; and to exclude also colloidal solution or dispersion; and finally, to exclude adsorption where there is a sort of quasi-union between the gas and the surface (so-called "adsorption compound"); for example, the adsorption of gases on charcoal or finely divided material, or on specially activated metal surfaces.

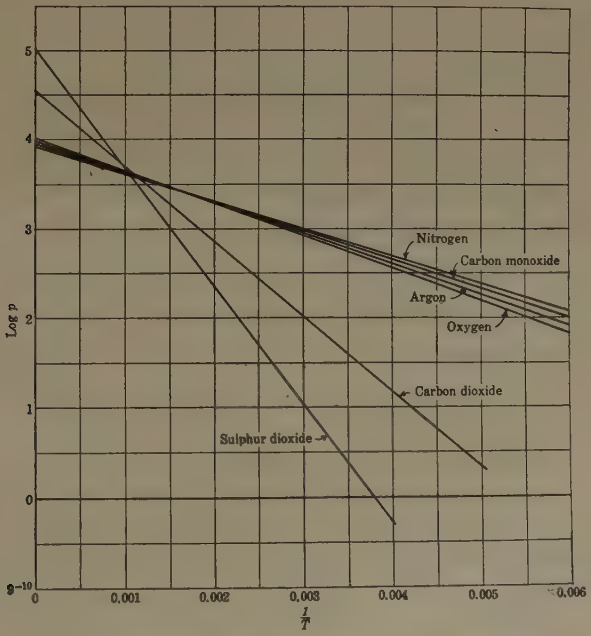

FIG. 1.—SATURATION PRESSURE (EXTRAPOLATED).

This should not be understood to mean that such a classification of degrees of chemical combination is actually proposed; it is used here because the simpler mass-law formulations of gas-solvent equilibria (Henry's Law or Nernst's Distribution Law) hold only for "simple solubility"; in the case of compound formation further consideration is required, while adsorption and dispersion do not follow the mass law. In other words, the argument is: The absorption of gases by hot metals is probably not a case of "simple solubility" and therefore the mass law or its equivalents cannot be applied without further justification.

Simple solubility has been much studied and there is a tremendous literature on methods for calculating the solubility of any substance in various solvents, but that problem is still an open one. Enough is known, however, to warrant the prediction that gases should have an almost negligibly slight simple solubility in molten metals at high temperatures, and it might be interesting to attempt an estimate of an upper limit for this solubility figure.

The method to be followed in making such an estimate is given by Hildebrand,[6] and consists, first, in obtaining the "ideal solubility" by plotting $\log p$ against $\frac{1}{T}$ from the data for the saturation pressures of the gases, and then extrapolating beyond the critical temperatures to the temperature desired (see pages 32–35 of Hildebrand's book for details); and, second, in correcting for the "internal pressure" by a method similar to the one used by Mortimer[7] for solids (see pages 113–116 of Hildebrand's book).

Fig. 1 shows the data for SO_2 and CO_2, and the lower extrapolated parts of the curves for oxygen, argon, carbon monoxide and nitrogen.[8] At $\frac{1}{T} = 0.001$ or 1000° K., these lines nearly all intersect at about $\log p = 3.60$, or $p =$ about 4000. Hence the "ideal solubility" at $1000° - 273° = 727°$ C. of any of the six gases shown on the graph in any molten metal at one atmosphere pressure is $\frac{1}{4000}$; that is, 1 mol of gas dissolved in 4000 mols of metal. (This is almost exactly one-fourth the "ideal solubility" at 20° C.)

To correct for "internal pressure," the values from Traube's calculations[9] given in the second column of Table 1 were used.

Methods for calculating internal pressure[10] give such widely varying results that the choice of the figures of Table 1 rather than some one of the other published sets can be justified only on the ground that Traube's table is the most extensive one and the only one giving data sufficient

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[6] J. H. Hildebrand: Solubility. Monograph, Amer. Chem. Soc. The Chemical Catalog Co., 1924.

[7] F. S. Mortimer: *Jnl.* Amer. Chem. Soc. (1922) **44,** 1416; Melting Point, Latent Heat of Fusion and Solubility. *Ibid.* (1923) **45,** 633.

[8] Data taken from Landolt-Börnstein: *Physikalisch-Chemische Tabellen* (1923) **2,** Tables 289 and 290.

[9] As given by W. C. McC. Lewis: Internal Molecular or Intrinsic Pressure—A Survey of the Various Expressions Proposed for Its Determination. *Trans.* Faraday Soc. (1911) **7,** 94–115.

[10] The absolute values for internal pressures are not known within wide limits. See Lewis' summary quoted above, or Chapter 9 of Hildebrand's book (footnote 6); or R. F. Mehl: Interatomic Forces in Metals and Alloys. *Proc.* Inst. Met. Div., A. I. M. E. (1928) 405–08.

TABLE 1.—*Relation of Solubility and Internal Pressure*

Substance	Internal Pressure, Atmospheres	Ratio of Solubility to Ideal Solubility	Solubility of Nitrogen per 100 Grams Solvent	
			C.c. (NTP)	Temp., Deg. C.
Octane	740	1.0000	19.5	20
Water	37,700	0.020	2.49	20
Mercury	34,400	0.022	0.25	20
Silver	125,700	0.0059	0.018	727
Copper	233,100	0.0032	0.025	727
Nickel	279,700	0.0026	0.025	727
Iron	319,700	0.0023	0.023	727

to test the relation between internal pressure and solubility for the list of gas solubilities given on page 131 of Hildebrand's book. For that particular series of solubilities ranging from "ideal" (in a liquid paraffin hydrocarbon) with an internal pressure of 740 atm., to water with about one-fiftieth of the "ideal solubility" at an internal pressure of 37,700 atm., the solubility coefficients as expressed by Hildebrand are roughly in inverse ratio to Traube's values for the corresponding internal pressures. Extending this simple rule of inverse proportions to the higher internal pressures of the metals gives the solubilities shown in column 4 of Table 1, expressed as cubic centimeters of nitrogen at normal temperature and pressure dissolved in 100 g. of the solvent at the temperature indicated.

There is no denying that the wide extrapolation in obtaining the "ideal solubility" may give an unreliable figure, and that the values of the internal pressure are not known with sufficient accuracy to lead to even a rough approximation of the solubility correction, and finally that making the solubility coefficients inversely proportional to the internal pressures rests on an insufficient basis. Nevertheless, it seems safe to say that the solubilities for nitrogen in the metals exhibited in column 4 of Table 1 (calculated to cubic centimeters of nitrogen per 100 g. of solvent, as an example), are still much too large, because, although the value 2.4 c.c., obtained for the solubility of nitrogen in water at 20° C. is at least of the same order as the actually observed value 1.5 c.c., the figure calculated for the solubility of nitrogen in mercury at 20° C., 0.25 c.c. per 100 g., or 1 c.c. of nitrogen in every 30 c.c. of mercury, is clearly much too large. There are no published figures for the solubility of gases in mercury, probably because the amount dissolved is too small to determine; otherwise, for instance, there would be no object in substituting mercury for water in gas-analysis apparatus or the like. In other words, the estimate for mercury is patently at least 100 to 1000 times too large, but this cannot be wholly the fault of the method of calculation employed, for then the value for the solubility in water should also be of different order. The explanation for the discrepancy must be sought in some neglected factor which may well be the dielectric constant.[11] The dielectric constant for ordinary liquids is from 4 to 6; water has the unusually high dielectric constant of 80; and metals are commonly considered to have an infinite dielectric constant as deduced theoretically by Maxwell. At first sight, these relations would appear to offer a way of further correcting the solubility of nitrogen in water and especially in mercury; but unfortunately the variation of solubility with dielectric constant follows no recognizable law, and furthermore, the dielectric constant of metals cannot be determined experimentally.[12]

The four solubility figures for nitrogen in metals at 727° C. (1000° K.) in column 4 of Table 1 are, as they stand, less than the experimental error claimed by Sieverts, Iwasé, Bircumshaw, or Steacie and Johnson. If then these figures are further reduced to less than one-hundredth of their present value, as it seems they should be by analogy with mercury, they fall so far out of the range of detection experimentally that they may be considered negligible.

The estimate thus made may then be stated as follows: The simple solubility of gases in molten metals at higher temperature, if not absolutely zero, is certainly less than the experimental error of modern precision laboratory methods.

A confirmation of this view may be found in the recent very careful work of Steacie and Johnson[13] who find

> no measurable absorption of nitrogen by silver between 200° and 800° C. If any absorption takes place it is certainly less than 0.002 volumes of gas per volume of silver. This is to be expected, as it has been found by a large number of observers that nitrogen is not absorbed by metals except in cases where a well-known nitride is formed.

And again in the summary of their paper, they say: "Nitrogen has been shown to be insoluble in silver."

This one instance would be sufficient to prove the point for, from what has gone before (see Fig. 1 for example, or the many instances to be found in Hildebrand's book) the "simple solubility" of gases in solvents is of the same order for all gases in any one solvent.

There are, however, a number of other recorded instances of insolubility of gases in metals. Sieverts[14] states that the noble gases (Ar,

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[11] Reference of footnote 6, 84–86, 131 and 136.

[12] At least one physicist has recorded his belief that the dielectric constant of metals is of the same order as for nonmetallic substances. See F. Sanford: *Phys. Rev.* [2] (1918) **12**, 130–135.

[13] E. W. Steacie and F. M. G. Johnson: The Solubility and Rate of Solution of Oxygen in Silver. *Proc.* Roy. Soc. (1926) **A 112**, 542–558.

[14] A. Sieverts: Die Aufnahme von Gasen durch Metalle. Given before the Deutsche Gesellschaft f. Metallkunde, June 24–25, 1928. Reported in *Stahl u. Eisen* (1928) **48**, 1251–52.

He, Ne, Kr and X) do not dissolve in metals. Furthermore, Sieverts had found previously that hydrogen was quite insoluble in cadmium, thallium, zinc, lead, bismuth, tin, antimony, silver, gold and aluminum, although Bircumshaw[15] could not confirm this for tin and aluminum, and Steacie and Johnson find about 0.47 c.c. hydrogen dissolved in 100 g. of silver. Iwasé's[16] values for the solubilities of hydrogen in tin and aluminum are even larger than Bircumshaw's but he gives extremely small values for hydrogen in zinc and antimony, although he finds no nitrogen dissolved in solid copper and only traces in liquid copper. The latter observation agrees with Stubbs' observation that passing nitrogen through molten copper does not change the freezing point.

Consequence of the Conception of Insolubility of Gases in Hot Metals

One of the most disturbing features of recent determinations of the solubility of gases in metals is the lack of agreement between the results of even the most careful and experienced investigators.

Thus Iwasé's figures differ materially at times from those of Sieverts, and he therefore feels that Sieverts must have failed to obtain equilibrium. Sieverts,[17] on the other hand, has repeated some of Iwasé's experiments and concludes that Iwasé's work must be in error. Krings and Kempkens,[18] in a very careful piece of work, get a value for the solubility of oxygen in solid iron that is higher than the figures given respectively by Oberhoffer[19] and by Wimmer,[20] but considerably lower than that of Schenck and Dingman,[21] and very much lower than that of Eastman and Evans[22] or of Matsubara.[23] Steacie and Johnson's maximum value for the solubility of hydrogen in silver at 800° C. is about one-half the figure given by Sieverts and others, and the solubilities of hydrogen in tin and aluminum as given respectively by Sieverts, Iwasé and Bircumshaw do not agree.

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[15] L. L. Bircumshaw: The Solubility of Hydrogen in Tin and Aluminum at High Temperatures. *Phil. Mag.* [7] (1926) 510–522.

[16] K. Iwasé: Solubility of Gases in Metals and Alloys. Abs., *Stahl u. Eisen* (1927) **47,** 1786–1889.

[17] A. Sieverts and H. Hagen: Bemerkungen zu dem System Eisen-Wasserstoff. *Ztsch. f. Phy. Chem.* (1931) **A155,** 314–17.

[18] W. Krings and J. Kempkens: Ueber die Loeslichkeit des Sauerstoffs in festem Eisen. *Ztsch. f. Phys. Chem.* (1929) **183,** 225–50.

[19] Oberhoffer, Scheffer, and Hessenbruch, *Stahle u. Eisen* (1927) **47,** 1540.

[20] Wimmer: Influence of Oxygen on the Physical and Technical Properties of Mild Steel. *Stahl u. Eisen* (1925) **45,** 73.

[21] R. Schenck and T. Dingman: Equilibrium Relations in the Reduction, Oxidation and Carbonization of Iron. VI, 7; Solubility of Oxygen in Iron. *Ztsch. f. anorg. u. allge. Chem.* (1928) 171, 239–57. *Ibid.* (1927) **166,** 113; (1929) **182,** 97.

[22] Eastman and Evans: Equilibria Involving the Oxides of Iron. *Jnl.* Amer. Chem. Soc. (1924) **46,** 888–903; *ibid.* (1929) **46,** 888.

[23] A. Matsubara: Chemical Equilibrium between Iron, Carbon and Oxygen. *Trans.* A. I. M. E. (1921) **67,** 3; *Ztsch. f. anorg. u. allge. Chem.* (1922) **124,** 39.

This is only a short list of the existing discrepancies, many of which may of course be explained by obvious imperfections in apparatus, such as in the extremely interesting and promising method recently used by Brace and Ziegler,[24] or by questionable interpretation of indirect methods, as in the use of metallographic analysis for determining oxygen in iron; but the cases cited above represent very recent work by experienced and competent experimentalists who have at their command all the refinements of modern laboratory technique, and who must have approached the problem fully cognizant of the minutest details of its many difficulties. Each one of these recent experimenters appears to have such confidence in his own work that he can conceive of a value differing from his own only as an error on the part of someone else, clearly on the tacit assumption that there must be one definite fixed solubility for each gas in each metal at a given temperature—an assumption that is not supported by the accumulated evidence of recent work.

If the "simple solubility" of gases in metals is indeed zero or at most too slight to be detected by modern methods, the variable results in the best recent work on the action of gases on hot metals should be attributable to factors that have not received adequate consideration. That this conclusion may not be as unorthodox as it seems at first sight appears from the following considerations.

Sieverts, Bircumshaw, and Iwasé, respectively, give for the solubility of hydrogen in tin at 800° C.: 0.00 c.c., 0.35 c.c. and 1.0 c.c. per 100 g. of tin. Reduced to mass, the two last volumes are, respectively, 0.000031 and 0.000090 g. of hydrogen dissolved in 100 g. of tin; or, say, 3 and 9 in 10 million parts by weight; or finally, expressed as atoms, 1 atom of hydrogen for 28,000 and 9300 atoms of tin, respectively.

Two recent values for the solubility of hydrogen in silver at 800° C. are 0.45 c.c. (Steacie and Johnson) and 0.73 c.c. (Sieverts) per 100 g. of silver, or 4 and 6.5 in 10 million parts by weight, respectively, or 1 atom of hydrogen respectively in 21,000 and 13,000 atoms of silver. Sieverts states[25] that at 1 atm. pressure, there is at most 10 atoms of nitrogen (at 700° C.) to 10,000 atoms of γ iron. The average amount of mixed gases (say of mean molecular weight 35) is about 8 c.c. in 100 g. of certain varieties of molten cast iron,[26] at 1270° to 1600° C., corresponding roughly to 1 atom of gas in 5000 atoms of iron (neglecting carbon, silicon, phosphorous and other slight admixtures).

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[24] N. A. Ziegler: Gases Extracted from Iron-carbon Alloys by Vacuum Melting. *Trans.* A. I. M. E., Iron and Steel Div. (1929) 428.

[25] A. Sieverts: Die Absorption von Stickstoff durch Eisen. *Ztsch. f. phys. Chem.* (1931) **A155**, 299–314.

[26] A. Wuester and E. Piwowarsky: Ein Neues Verfahren zur Bestimmung des Gesgehaltes von fluessigen Metallschmelzen. *Stahl u. Eisen* (1927) **47**, 698–702.

The reason that such extremely small amounts can be detected at all is that the volumes of gases in general, and of hydrogen in particular, are enormous compared to their masses. When dealing with gases dissolving in water and in organic solvents at ordinary temperatures, statistical kinetic equilibrium between the gas phase and the solution, even in the extreme cases of 1 to 25,000 or more atoms, is maintained in virtue of Henry's law, as is amply demonstrated by the degree of conformity attained by different observers in their determination of the solubility of gases in liquids at ordinary temperatures. It happens that the solubility of gases in liquids, especially in water, at ordinary temperatures is of the same order as the volumes of gas absorbed by molten metals, and this coincidence has probably helped to obscure the fundamental difference that exists between ordinary liquids and molten metals as solvents.

Most of the recent investigators of the solubility of gases in metals apparently have been more or less conscious of this difference and some of them have actually sought a new explanation for this solubility. Thus, Steacie and Johnson in their two papers on the solubility of hydrogen and oxygen in silver (quoted frequently on the preceding pages) were evidently struck by the positive temperature coefficient for gas-in-metal solubilities as contrasted with the negative temperature coefficients for gas-in-ordinary liquid solubilities[27] and, finding an explanation for this fact in terms of Langmuir's[28] formulation for the adsorption of gases by metals, were led to study the subject along the lines that have proved so fruitful in explaining the action of metals at moderate temperatures in catalyzing gas reactions.[29] Steacie and Johnson's summaries emphasize this relation of gas absorption to adsorption and to diffusion[30]

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[27] The force of this argument for a difference between the two types of gas solutions is weakened considerably by G. Tammann's theoretical deduction (*Ztsch. f. Elektrochem.* (1927) **35,** 425–428) showing that solutions of gases in ordinary liquids need not necessarily have a negative temperature coefficient, and this weakening is much increased since Tammann has been able to illustrate his deduction quantitatively for the solubilities of argon, helium, and neon in water and organic liquids as determined by Lannung (*Jnl.* Amer. Chem. Soc. (1930) **52,** 73).

[28] I. Langmuir: *Jnl.* Amer. Chem. Soc. (1916) **38,** 2221.

[29] The literature on this subject is too vast to abstract. A suitable presentation of the main facts is given by H. S. Taylor: Chemical Reactions at Surfaces. *Chem. Rev.* (1931) **9,** 1–46.

[30] On diffusion of gases through metals, see for example, G. Deming and B. Clifford Hendricks: The Diffusion of Hydrogen through Metals. *Jnl.* Amer. Chem. Soc. (1923) **45,** 2857–64.

F. M. G. Johnson and P. Larose: Diffusion of Oxygen through Silver. *Jnl.* Amer. Chem. Soc. (1927) **49,** 312–26; *ibid.* (1926) **46,** 1377; see also Chem. Abs., **18.**

G. Borelius and S. Lindblom: The Diffusion of Hydrogen through Metals. *Ann. d. Phys.* (1927) **82,** 201–26.

W. E. Deming: *Phil. Mag.* (1928) **5,** 1080.

Footnote continued on next page.

which leads them to say: "It appears probable that the absorption of gases by metals is only a particular case of a much more general phenomenon."

So also, Lewis,[31] led probably by the usual interpretation of Sieverts' $\sqrt{p}$ law, proposed the theory that the ability of a metal to dissolve gas depends on the ability of that metal to dissociate the gas.

Such explanations of the gas-in-metal solubility tend in the right direction but they do not go far enough. It is true that metals have the unique structure that Langmuir calls "giant molecules," over which there may be superposed a secondary "block" structure,[32] and that these secondary blocks may persist even above the melting point, as Prof. Alexander Goetz, of the California Institute of Technology, believes he has observed;[33] and, furthermore, one would naturally expect liquids of high internal pressure and, if not cf high dielectric constant, certainly of considerable electrical conductivity (*i. e.*, free electrons) to exhibit a strong ionizing power on solutes, and all these things must have some relation to the interaction of such liquids (molten metals) with gases. It seems but a logical step to postulate that the action of gases on hot metals should be explicable in considerable detail in terms of the electronic structure of the metals and gases, as is done by chemists with great success in connection with valency, where the formation of ordinary chemical compounds, of so-called "double salts," of the "coordination compounds" that formerly were so puzzling, and even of "adsorption compounds," all appear as slightly different modes of action of directed forces exerted by the fairly well established electronic configurations of the outer rings of the separate atoms.

Direct confirmation of this postulate is afforded by Sieverts'[34] table of the "hydrides" of the metals in relation to the periodic law. The work on atomic structure has demonstrated that any property or reaction that can be correlated with the position of the elements as arranged in the periodic table is explicable in detail as an electronic phenomenon. It remains for someone to carry through this indicated electronic interpretation of Sieverts' table, and to extend it to the "oxides" and "nitrides," etc., of the metals.[35]

V. Lombard: Experimental Researches on the Diffusion of Hydrogen through Nickel. *Jnl. d. Chim. Phys.* (1928) **25,** 501–30, 587 or *Rev. de Mét.* (1929) **26,** 343.

G. Valensi: *Jnl. d. Chim. Phys.* (1929) **26,** 152–77, 202–18.

[31] W. C. McC. Lewis: *Jnl.* Chem. Soc. (1920) **117,** 623.

[32] F. Zwicky: Zur Mosaikstruktur der Kristalle. Helvetica Phys. *Acta* (1930) **3,** 269; (1930) **4,** 50; *Proc.* Natl. Acad. Sci. (1929) **15,** 253, 816; (1930) **16,** 211.

[33] Private communication.

[34] A. Sieverts: Die Aufnahme von Gasen durch Metalle. *Ztsch. f. Metallk.* (1929) **21,** 37–46; abs., *Metall u. Erz,* **26,** 548–550.

[35] N. V. Sidgwick: The Electronic Theory of Valency. Oxford University Press, 1929. This would be an excellent guide in working out such an interpretation.

If the absorption of gases by molten metals is indeed an electronic phenomenon, the amounts of gas absorbed in any given case ought to be profoundly influenced by anything that causes ionization of the gas. That hot metals emit ions[36] has been known for a long time, and, although the ionization is somewhat capricious,[37] the effect is not small, and is as easily measurable as is, for example, the trifling amount of hydrogen absorbed by molten silver or tin.

Furthermore, at 1000° C., ordinary gases themselves begin to be ionized by thermal forces alone, and this action added to the ionization of the gas by the thermions from the hot metal might produce effects[38] sufficient to explain deviations of the order of 1 atom of gas in 10,000 or more atoms of metal such as characterize the discrepancies that appear in the comparison of the best results obtained by Sieverts, Steacie and Johnson, Bircumshaw and Iwasé. To anyone who has had experience with the ionization of gases, the possibilities of an influence of the size mentioned resulting from a change in the shape of the containing vessel or its gas space, from variations in length or diameter of connecting tubes, from accidental conducting surfaces in glass and other material, from extent of hot metal surface, or even from less obvious factors, will be quite real; in fact, these effects are so well known to physicists that failure to consider them hitherto in experiments on the solubility of gases in hot metals must be ascribed to the influence of the supposed analogy between liquids and molten metals as solvents for gases.

The most important consequence, then, of the recognition of the "insolubility" of gases in hot metals is the need for a general principle on which to base predictions as to the various degrees of "chemical combination" encountered in the interaction of the various gases with hot (molten) metals. It is pointed out that an electronic theory, patterned after the chemists' electronic theory of valency, holds out hope of offering a successful detailed description of the phenomena encountered in this field. It is suggested, also, that consideration of possible thermionic effects might account for the discrepancies existing in recent determinations of the "solubilities" of gases in molten metals.

To give an explicit example of one type of intimate structure of metal-gas systems which could be predicated on the above considerations, we may think of a gas as ionized at the metal surface and the ionized gas then absorbed at the interfaces of the "giant" molecules or blocks of the mosaic structure. With metals no experimental proof of the existence of such a metal-gas system is available; however, Gross and St. Clair[39] have shown that the amount of hydrogen sulfide taken up by unit surface of galena becomes less as the size of the cubes approaches a figure of about 2μ, indicating that the hydrogen sulfide is taken up between unit cubes of the order of 2μ diameter.

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[36] O. W. Richardson: The Emission of Electricity from Hot Bodies, 2nd Ed. New York, 1928. Longmans, Green & Co.

[37] J. A. Harker and G. W. C. Kaye: *Proc.* Roy. Soc. (1913) **A88**, 522–38.

[38] Especially if there is formation of Langmuir's well-known active hydrogen, or Strutt's active nitrogen, or the like.

[39] U. S. Bureau of Mines *Rept. of Investigations.*, not yet published.

Finch and Stimson[40] conclude that a gas can be held in at least five different ways on a hot metal surface:

(i) The gas is held physically in an electrically neutral condition, in the form of a condensed layer which even at 850° is, as has been shown by Langmuir (*Trans.* Faraday Soc. (1922) **17,** 607) at least of monomolecular thickness.

(ii) The gas is held loosely in an electrically charged condition, whereby the surface itself acquires a charge, which can be removed with complete restoration of the in vacuo charge proper to the surface within 30 to 60 minutes by evacuation at 850°. As examples may be cited H_2, N_2, CO, CO_2, H_2O and Ar, in the case of gold; N_2 and Ar, in the case of silver; (no experiments were carried out with this metal in contact with CO, CO_2 or H_2O); and all these gases together with oxygen, but excepting carbonic oxide, in the case of nickel.

(iii) The gas is held more firmly than in (ii) in a condition approximating to unstable, loose chemical combination; for example, O_2 on gold, and O_2 or H_2 on silver. In these cases the respective gas charges can only be removed with difficulty, and the necessary time of evacuation increases with the time during which the surface was previously in contact with the gas.

(iv) The gas is held in a still firmer manner than as outlined in (iii); the surface, however, continues to exhibit the charge characteristic of the gas in question even after prolonged evacuation. The one example of this type of combination so far revealed in the course of this investigation is that of carbonic oxide on nickel.

(v) The gas is bound chemically to the surface and the resulting stable chemical compound undergoes no dissociation at temperatures up to 850°. In this case the in vacuo charge on the oxidized surface is the same as the in vacuo charge characteristic of the reduced oxygen-free surface. The one example which we have so far been able to study is that of oxygen on nickel, where direct evidence was obtained, not only of compound formation (absorption of a large volume of oxygen by the hot surface, coupled with the change of appearance at the surface from a bright metallic lustre to a matt greenish-black), but also of the stability of the nickel oxide at 850°. Thus the oxygen, when once it is firmly chemically combined with nickel, does not give rise to the charge otherwise characteristic of that gas.

Metallurgical Applications

One interest of practical metallurgists in a theory of the absorption of gases by metals is the hope of getting an insight into possible connections between the remarkable change in properties of metals and the minute contents of gas.

The tendency to attribute almost every unexplained physical property of metals to the influence of gases has been overdone, and has been deplored by Fraenkel[41] who, however, at the same time points out that at the moment this tendency has not only been checked but has been discouraged more than is desirable as a result of the claim of four Frenchmen[42] that there is no connection between the properties of electrolytic iron and its hydrogen content—the one instance that has hitherto been regarded as the most authentic case of a parallelism between gas content and the properties of hardness and brittleness. Under the conditions, it will be wise to refrain from further comment on this phase of the subject, and to limit ourselves to a discussion of the prevention of blowholes in casting metals.

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[40] Finch and Stimson: *Proc.* Roy. Soc. (1927) **A116,** 379.

[41] W. Fraenkel: Ueber den Einfluss kleiner Beimengungen in Metalle. *Ztsch. f. Metallk.* (1931) **23,** 221–24.

C. J. Smithells: Impurities in Metals.

There is no doubt that practical metallurgists approached the problem at first from the conviction that here was a case analogous to the solubility of gases in water; all that was needed was to know how much gas would dissolve in the liquid. The symposium on the occlusion of gases by metals, presided over by R. Hadfield in 1918[43] was dominated by this point of view, or rather by the first struggles to get away from this point of view, as is evidenced by the prominent place given the discussion of the "spitting" of silver, then regarded as a most strange and unusual way for a solution of gas to behave. It may be mentioned incidentally that Roozeboom, 14 years earlier, had indicated a way, simple to one versed in phase-rule diagrams, of clearing up this mystery.[44] The phase-rule method has not been followed much since, although it would be illuminating qualitatively; quantitative results would probably be unreliable because the conditions of equilibrium given by the phase rule are valid only "when uninfluenced by gravity, electricity, distortion of the solid masses, or capillary tensions."[45]

Metallurgists soon found that the gas-in-water analogy was not helpful in actual operations, and their efforts to overcome difficulties caused by gases were prompted by necessity and not guided by theory. The presence of impurities in commercial metals makes the view suggested in the earlier parts of this paper—that gas absorption and evolution is of necessity always a case of chemical reaction—much more natural than it is with pure metals in the laboratory. Hence the problem to the practical metallurgist is not to answer the question, What causes the gas to dissolve?, but the question, What prevents immediate and almost explosive reaction between such things as $2Cu_2O + Cu_2S = 4Cu + SO_2$; and $FeO + Fe_3C = 4Fe + CO$?

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[42] Guichard, Clausmann, Bitlon, and Lanthony: *Compt. rend.* (1931) **192,** 623.

[43] *Trans.* Far. Soc. (1918–19) **14,** 173–191, contains many papers on gases in metals, a long discussion and a bibliography up to 1918 with 73 titles.

[44] H. W. B. Roozeboom, in Die Heterogenen Gleichgewichte (1904) **2,** 355, says, "Recently it has been shown frequently that molten metals dissolve gases, chiefly oxygen, probably because of the formation of an oxide in the liquid mixture. This depresses the melting point noticeably, for example by 20° and 16° for Ag and Cu heated in air. The solution is then saturated with oxygen at a pressure of ⅕ atmosphere. This pressure, in the case of silver, is lower than the maximum pressure of the triple-curve, because on cooling, silver crystallizes out with separation of oxygen (spitting of silver). That is, this phenomenon takes place at that temperature which has been called 'the second boiling point' above. The liquid silver under active ebullition decomposes into solid silver and gaseous oxygen."

[45] J. W. Gibbs: *Trans.* Conn. Acad. (1876) **5,** 115. Oversight of these limiting conditions may explain the failure of satisfactory agreement in many of the ambitious attempts to apply the mass law and Clapeyron's equation to supposed equilibria in metallurgical reactions; for example, the most recent studies by F. Sandelin: A Study of the Velocity of Reaction and Equilibrium Conditions of Steel. Jernkontorets Ann. (1929) 519–44, or *Metals and Alloys,* **1,** 475; and E. Ameen and H. Wilners: A Study of Gases in Liquid Steel. Jernkontorets Ann. (1928) **83,** 195–265.

An ingenious answer to this puzzle has been offered by C. S. Witherell,[46] who suggests that if either the cuprous oxide or cuprous sulfide adsorbed an inert film (*e. g.*, nitrogen) the necessary actual contact between oxide and sulfide would be prevented and hence no reaction could take place. Another explanation, and one that has the advantage of requiring no additional hypothesis, is suggested by the curious behavior of gas-free liquids reported by Meyer.[47] Meyer's "negative pressure" is nothing else but the internal pressure on which we based our contention of "insolubility" of gases in molten metals. The argument may be put most simply in some such terms as the following: If a high internal pressure tends to squeeze out foreign substances (solutes or gases) and thus prevent their dissolving, then, conversely, any reaction producing gas could not take place within such a liquid without first overcoming the tremendous internal pressure. Bircumshaw, on finding that hydrogen could not be completely pumped out of molten aluminum even in 114 hr., explained the same phenomenon in terms of surface tension, which is in essence again the same as our explanation, because internal pressure and surface tension are fundamentally interrelated. In other words, if the gas formed by the product of the reaction could be evolved into a space free from the high internal pressure of the molten metal, the reaction could proceed normally. This suggests bubbling SO_2 through copper or CO_2 through iron to make the two reactions cited above run to completion.

This novel method for removing dissolved gases is mentioned by Smithells[48] as having been discovered by Arbuthnot,[49] who, at the suggestion of Rosenhain, tried bubbling nitrogen through aluminum and found it effective. So, too, Pryterch[50] reports success in degassing copper by bubbling nitrogen through it. To this list Tullis has added chlorine and boron trichloride for aluminum alloys.

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[46] Discussion of A. E. Wells and R. C. Dalzell: A Theory Concerning Gases in Refined Copper. *Trans.* A. I. M. E., Institute of Metals Div. (1930) 361.

[47] J. Meyer: Zur Kenntniss des negativen Druckes in Fluessigkeiten. *Abh.* d. Deutsch. Bunsen Gesellschaft (1911) **3,** No. 1.

[48] C. J. Smithells: Gases in Metals. *The Metal Industry* (Mar. 6, 1931) **38,** 268.

[49] Arbuthnot: *Jnl.* Inst. Metals (1925) **33,** 233–234.

[50] W. E. Pryterch: *Jnl.* Inst. Metals (1930). *Preprint* No. 516.

One would think also of providing an interface as a means of inducing bubble formation to facilitate the two reactions under discussion, and this is probably the explanation for the success of the method called "presolidification" by Smithells, or "slow solidification" by Pryterch.

The third method mentioned by both Smithells, and Pryterch—vacuum melting[51]—seems to work well enough to be applied to the commercial production of a small but definite volume of metals for special purposes, although the last portions of gas resist with surprising tenaciousness removal by a vacuum.

There remains still to be considered the relation of the conception of gas solubility to the application of physical chemistry to metallurgy, which is to say, the explanation of metallurgical reactions in terms of the mass law. Taking as an example the mass law expression for the reaction

$$\mathrm{FeO} + \mathrm{C} = \mathrm{CO} + \mathrm{Fe},$$

which is usually written

$$K = \frac{\mathrm{CO}}{(\mathrm{FeO})(\mathrm{C})},$$

and which according to Larsen[52] may be expressed as

$$K^1 = \frac{1}{(\mathrm{FeO})(\mathrm{C})}.$$

This assumption of a constant and finite solubility of the carbon monoxide was first made by LeChatelier, whose brilliant work and that of his followers, notably Styri, is so well known to metallurgists that detailed reference may be omitted here. It is pertinent to suggest, however, that the discrepancies between theory and fact that have remained even after much careful work in this field might possibly be a consequence of this particular form of assumption for the solubility of carbon monoxide in iron.

It is quite true that so far as the application of the mass law is concerned an exceedingly small solubility is sufficient provided it be constant. It would be difficult indeed to prove or disprove the existence of such an infinitesimal solubility. However, for practical purposes, if this solubility is not so great as to considerably outweigh other forms of gas-metal contact as a means of reaction, the mass law cannot be fruitfully applied. In the foregoing an attempt has been made to show that other forms of gas-metal contact which do not follow the mass law very likely exist to such an extent that simple solubility is an insignificant factor.

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[51] See also A. Villachon et G. Chaudron: Sur la teneur en hydrogene et en ca oxyde de carbone de quelques metaux fondus dans le vide. *Compt. rend.* (1929) **189,** 324.

W. Rohn: Technische Eigenschaften Vakuumgeschmolzener Metalle. *Ztsch. f. Metallk.* (1929) **21,** 12–18.

[52] B. M. Larsen: Origin and Effect of Inclusions in Steel. *Metals and Alloys,* (1930) **1,** 703.

For example, the maximum "physical" solubility we can postulate for a gas-metal system is certainly something less than 0.001 c.c. per 100 g. of metal, as indicated by previous discussion. A simple calculation will show that if only $\frac{1}{10}$ c.c. of gas is distributed through this 100 g. of metal in the form of bubbles of 10μ dia. the number of gas molecules in contact with metal will be much larger than the number that can dissolve. Since in all these reactions there is a large evolution of gas, we are still not permitted in any practical case to take the CO concentration—or activity—if you wish, as proportional to the partial pressure.

It therefore appears that before we can fruitfully apply the mass law to gas-metal systems we must know something of the intimate structure of such systems.

SUMMARY

1. An approximate computation has been given to show that the simple solubility of gases in molten metals is, for all practical purposes, zero.
2. It has been suggested that an electronic explanation for the various degrees of tenacity with which gases are held by metals is demanded by Sieverts' periodic table for the interaction of hydrogen with the elements.
3. Attention has been drawn to the desirability of considering thermionic effects in any study involving hot metals.
4. A simple explanation has been offered for the apparent paradox that the reaction in such systems as cuprous oxide-cuprous sulfide in molten copper do not react explosively.
5. The necessity of a knowledge of the intimate structure of gas-metal systems before the mass law may be applied to them is emphasized.

Solubility of Gases in Metals*

By V. H. Gottschalk† and R. S. Dean,‡ Washington, D. C.

(New York Meeting, February, 1932)

Abstract

In the theoretical study of metallurgical reactions, it is necessary to make certain assumptions concerning the nature of metal-gas systems. The assumption usually made is that the reaction in such systems takes place predominantly with gas that is in "solution" and that the amount of solution follows the rules which have been developed for aqueous solutions; namely, Henry's law. The purpose of this paper is to inquire whether these assumptions are the best ones that present knowledge of gas-metal systems permits us to make.

In the first part the extent to which a gas will dissolve in a metal and still follow Henry's law is considered. The conclusion is believed justified that the number of molecules of gas that can dissolve in a metal and have the system follow Henry's law must be small indeed. It is therefore improbable that the first assumption concerning the predominance of these dissolved molecules in reaction is correct. It is suggested that some improvement in the correlation of the probabilities with the assumptions made in the mass law equations would be made by the use of the $\sqrt{p}$ law of Sieverts in place of Henry's law. However, the amount of gas that may be held in a metal so that it follows either Henry's or Sieverts' law is considerably outweighed in most metallurgical reactions by that held in gas-metal systems of entirely different structures and concerning which little experimental evidence is available. Some speculation concerning the nature of these is offered. The conclusion is that attention should be given to the determining of the nature of gas-metal systems and that the really fruitful application of the mass law and its connected calculations will have to await a more complete knowledge of these systems than we now possess.

DISCUSSION

(Paul D. Merica presiding)

P. D. Merica, New York, N. Y. (written discussion).—The solubility relations of gases in metals, in so far as they are known from the pioneer work of Sieverts and others, have from the first presented certain challenging peculiarities. The authors have emphasized the significance of these characteristics and suggest that they point to some sort of chemical or other combination of these gases with metals during solution. With this conclusion we must be in complete accord.

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* This paper is available at the office of the Institute as a *Preprint*.

† Senior Physicist, Metallurgical Division, U. S. Bureau of Mines.

‡ Chief Engineer, Metallurgical Division, U. S. Bureau of Mines.

Now there are two practical aspects of their views which I think deserve mention. In the first place, the temperature coefficient of "apparent" solubility as revealed by available reports is not only of the wrong sign to be in accord with the view that this solubility is of the "simple" variety, but it is too large as well. The simple "geometrical" troubles we encounter in consequence of gases in metals are due to variation of solubility with temperature and with state of aggregation. If simple solubility were the rule in gas-metal systems, we should have a much smaller temperature variation of solubility, and our gas-hole and similar difficulties would be much reduced.

The fact that gas solubility apparently involves chemical reaction and combination also suggests the reason why gas absorption and rejection in metals should be so sensitive to chemical composition of the solvent metal or alloy. "Simple" gas solubility should not be much affected by small quantities of impurities in metals. But "apparent" solubilities, depending on chemical reaction with the atoms of the solvent, can obviously be profoundly affected by slight changes in the character of the solvent—and our practical experience is thus in accord with the authors' views in suggesting this abnormal sensitivity of gas solubility to variations in metal composition.

The conclusion of the authors that in order to understand gas-metal relations better we must seek means of developing further information concerning the nature of the gas-metal compounds formed during gas absorption cannot be too strongly emphasized.

E. R. Darby, Detroit, Mich.—We have done considerable work with copper, tin and lead alloys and we have found that the gases causing the greatest difficulty are those resulting from the reduction of oxides. When the metal is cast, the sand cores become heated. Any oxides present in the metal next to the core are reduced and gases are given off which produce holes in that portion of the casting. We think that lead oxide is reduced in this cycle.

H. D. Hibbard, Plainfield, N. J. (written discussion).—In considering the gases of steel there are seven cases or fields to be examined: (1) those in the charge materials; (2) those encountered in melting and working; (3) those evolved in the mold; (4) those in the gas holes in the ingot; (5) those evolved when the cold steel is drilled; (6) those evolved when the metal is heated and (7) those evolved when the metal is again melted. These are all different and knowledge of all may be essential. Then each of these seven fields must be considered in relation to the others and also under all the variations of the accompanying conditions.

Having determined the gases and their effects, the problem becomes: first, to minimize the quantities of the harmful gases entering the metal; second, to eliminate them as fully as possible, and third, to neutralize the harmful effects of those persisting in the metal. The matter is so huge that its study may never be completed, in all its refinements, but useful knowledge may come from even moderate investigations and research. Hydrogen is probably the most troublesome gas and should be the first to be studied.

In a rimming or effervescing steel ingot there are usually three distinct sets of gas holes: (1) skin holes near the outer surface, which are caused by hydrogen; (2) intermediate holes, in a zone parallel to the surface and well inside the skin holes, which are formed by carbon monoxide, and (3) central holes, which are thought to be caused by nitrogen or ammonia. To make rimmed steel regularly without skin holes is for the future. It has been done, though rarely.

F. R. Hensel, East Pittsburgh, Pa.—Recent experiments carried out by M. G. Mahoux[1] have shown that the diffusion rates of gases are greatly increased when the test specimen is subjected to high-frequency oscillations. We have undertaken research in this direction and hope to present some data soon. For our experiments we are using ultra sonic waves, which can be produced with either piezo-electric vibrations in quartz or magnetostrictive vibrations in ferromagnetic substances. We are using piezo-electric vibrations.

The motions set up are in some respect similar to thermal motions at very high temperatures. The difference is, of course, that in the sound waves the motions are ordered and can be controlled more readily than heat motions, which are at random. Our preliminary plans are to study the effect of ultra sonic waves on: (1) The absorption and removal of gases and other substances from metals; (2) the production of equilibrium distributions; (3) age-hardening phenomena; (4) removal of strains; (5) recrystallization; (6) permeability and hysteresis; (7) electrical resistance.

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[1] *Compt. rend.* (1930) **191**, 1928.

The Degassing of Metals*

By F. J. Norton† and A. L. Marshall,† Schenectady, N. Y.

(New York Meeting, February, 1932)

Abstract

To determine how rigorous a treatment was necessary completely to remove sorbed gases from molybdenum electrodes in vacuum tubes, the degassing process in high vacuum was studied in the temperature range 800° to 2300° C., and the gases analyzed. Some work was also done on the degassing of tungsten, nickel, and carbon. It was shown that the amount of gas is proportional to the mass of the sample and not to the surface area, indicating that the gas is distributed through the body of the metal. A study was made of the solubility of nitrogen in tungsten and molybdenum from 1200° to 2400° C., at equilibrium pressures from 0.01 to 760 millimeters.

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* This paper is available at the office of the Institute as a *Preprint.*

† General Electric Co.

PREPRINT.—American Institute of
Mining and Metallurgical Engineers

The Degassing of Metals

BY F. J. NORTON* AND A. L. MARSHALL,* SCHENECTADY, N. Y.

(New York Meeting, February, 1932)

THE object of this investigation was to make a comprehensive study of the degassing of molybdenum in order to determine how rigorous a treatment was necessary to completely remove sorbed gases from molybdenum electrodes in vacuum tubes. Some work has also been done with tungsten, nickel and carbon. As a logical development of this work it has been shown that the gas is present throughout the body of the metal and a study has been made of the solubility of nitrogen in molybdenum and tungsten and the rate of diffusion of nitrogen through molybdenum has been calculated.

Tests were made on molybdenum from all the commercial sources and no difference was discovered in the nature of the gases present, the amounts or the ease of removal. The reason for this was apparent when a study was made of the manner in which gases are absorbed by gas-free molybdenum. It is necessary to heat molybdenum to 1760° C. in a vacuum of the order of 0.001 micron for a time which varies lineally with the thickness, in order to obtain a condition in which no further gas is evolved by the sample. A sample so degassed can be handled and subsequently assembled in a tube and then degassed readily. The gases obtained from molybdenum are carbon monoxide and nitrogen, the nitrogen being the more difficult to remove.

APPARATUS AND TECHNIQUE

The apparatus is shown in Figs. 1 and 2. It consisted of two units, a degassing system and an analytical system. Each had a bake-out oven, as shown surrounding the systems in the sketches. The system will be traced, starting from the sample in the degassing system.

The samples made from sheet molybdenum were in the form of rings 7⁄8-in. outside diameter with a 7⁄16-in. hole in the center, and were from 20 to 250 mils (0.020 to 0.250 in.) thick, most of them being about 70 mils thick. There was a hole in the ring by which it was attached to a 100-mil molybdenum rod. This rod was threaded at one end and two molybdenum nuts held the sample in position. It was necessary to file three longitudinal grooves in the threaded end of the rod to prevent the nuts from sticking after the high-frequency heating.

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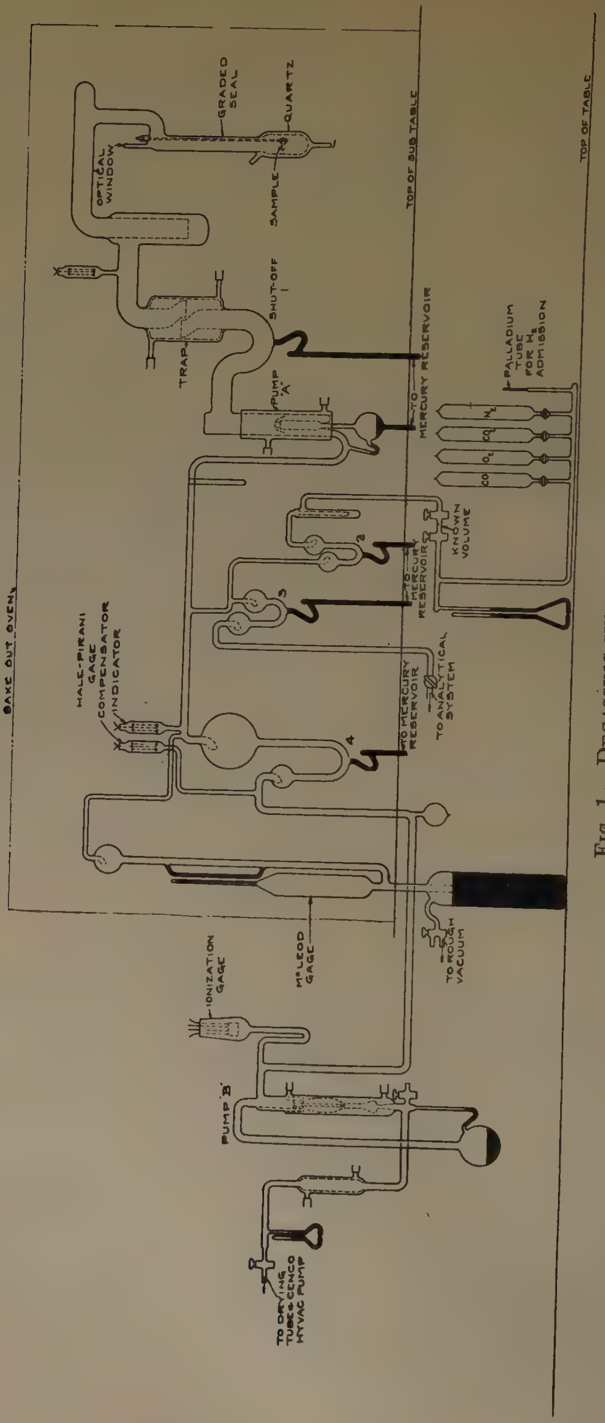

FIG. 1.—DEGASSING SYSTEM.

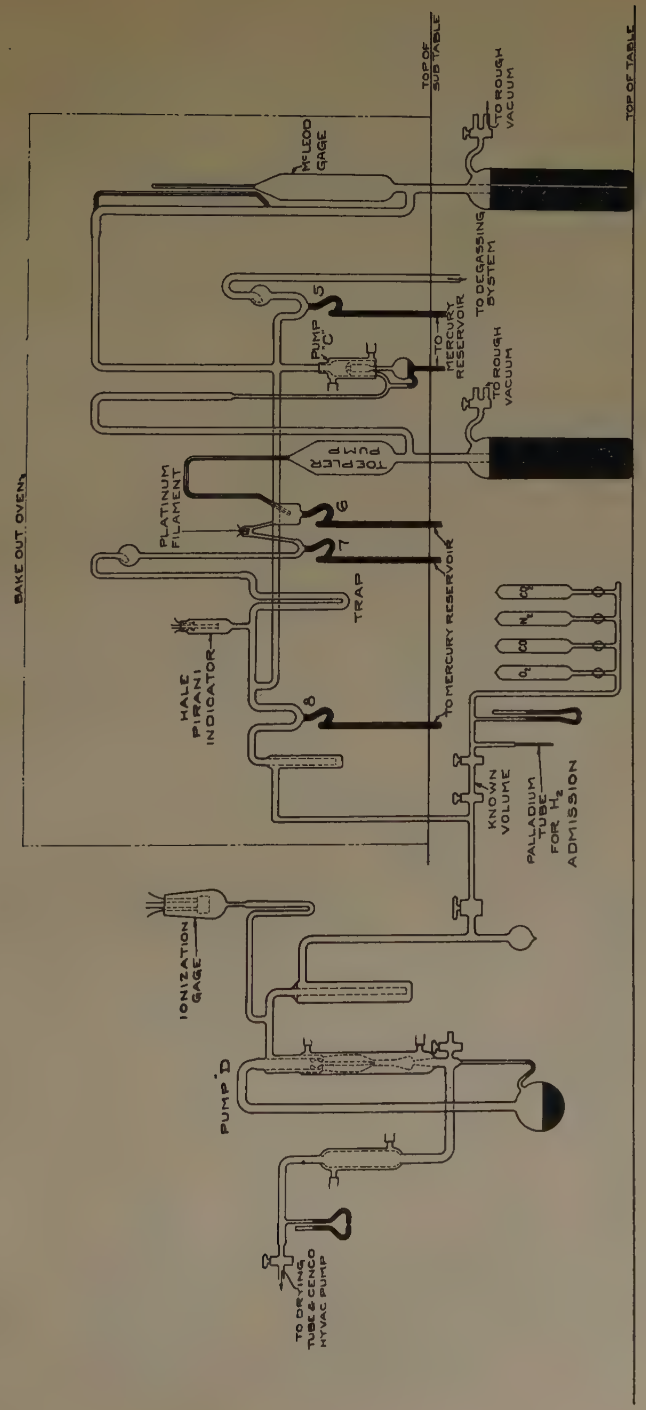

FIG. 2.—ANALYTICAL SYSTEM.

A water-cooled quartz chamber surrounded the sample. The high-frequency coil, which heated the sample, extended only around this chamber and was cooled by an air blast. High-frequency power of 1800-meter wave length was obtained from a self-rectifying oscillator circuit with a maximum power input of 20 kw. A graded seal connected the quartz to the rest of the apparatus, which was of hard glass. The temperature of the molybdenum sample was observed by an optical pyrometer through an optical window about 40 cm. distant from the sample. Since the object viewed under these conditions was not a black body, true temperature was not observed, but the so-called "brightness temperature." The correction of this to true temperature is discussed in a later section.

The apparatus was taken apart just above the graded seal; the quartz chamber was slipped off, washed with nitric acid, water and alcohol, and dried by an air stream. The old sample was removed by unscrewing the lower nut, and the new one was put on. Great care was taken not to handle any of the metal parts.

The apparatus was then sealed together again and evacuated by pump *B*. The mercury in the various traps was let down below the level of the bake-out oven. It was essential to attain a good vacuum before applying heat; otherwise the sample would become badly oxidized. Liquid air was put on the ionization gage trap. A small tube furnace extended over the quartz bulb, and a large bake-out oven extended over this and the whole system. The quartz was baked out at 800° C., reaching this during the last half hour of bake-out. The whole system was baked out at 450° to 470° C. for 1 hr. After cooling, the mercury was let up into pump *A* and traps 2 and 3 were closed. Cooling water was let into the pump *A*, trap and quartz jacket, and the pump started. At this point, the ionization gage showed a vacuum of better than 0.001 micron. Previous work had also shown that with this design and bake-out procedure no liquid air was needed on the large trap. This enabled the condensible gases CO_2 and H_2O to be determined, though the determination of H_2O would have been problematical because of the avidity with which it is absorbed by baked-out glass. The water-cooled trap kept the mercury pressure low enough in the quartz chamber so that no glow discharge in mercury vapor occurred during heating of sample with high frequency.

The preceding bake-out gave conditions such that less than 0.02 cu. mm. of gas was collected with shut-off 4 closed and pump *A* running, over a period of 10 to 15 min. This has been found to hold even when the sample and quartz were at 800° C. Consequently, it is evident that the gases later evolved could come only from the sample. A poor bake-out was indicated by a slow, continuous evolution of gas. The test of collecting less than 0.02 cu. mm. of gas as measured by the McLeod gage was applied before every run.

DETAILED MANIPULATION

On making a run, shut-offs 4, 3 and 2 were closed, and with pump *A* running, high-frequency heating was applied to the sample. As the gas was given off and collected back of pump *A*, the pressure was measured on the McLeod and the Hale Pirani gages. The latter was arranged as shown, so that the compensator was under a constant good vacuum.

When gas evolution apparently had ceased, the high frequency was shut off and pump *C* in the analytical system was started. This whole system had previously been baked out and evacuated, the large glass stopcock between the systems being open in the process. Shut-offs 8, 7 and 6 were closed, and when shut-off 3 was opened the gas sample was drawn over into the analytical system. The Toepler pump was operated during this time to reduce the back-up pressure of pump *C*.

After the sample of gas had been transferred, shut-off 3 was again closed and with a low pressure in the collecting end of the degassing system (0.01 to 0.03 microns) the high frequency was started again, to be sure that no more gas was being given off. This procedure was used because of the greater precision of the McLeod in the lower pressure ranges, for small quantities of gas.

The glass stopcock between the systems was then closed, as was shut-off 5, isolating the two systems. The degassing system was then available for another run. The sample of gas was in contact with mercury and baked-out glass only, except for the brief passage through the glass stopcock during its transfer, which reduces to a minimum the possibility of contamination.

The volume of the collecting part of the degassing system was determined by admitting dried nitrogen to the system with pump *A* operating. The volume of the McLeod gage was known from its calibration. Mercury was let into the gage, trapping off a known volume of gas at a measured pressure; the rest of the collecting system was evacuated, shut-off 4 closed again, the nitrogen in the gage admitted to the system and the pressure again measured. The ratio of the two pressures times the volume of the gage gives the volume of the collecting system.

ANALYTICAL TECHNIQUE

The method was essentially that of Langmuir[1] for the analysis of small amounts of gases.

As described above, the sample was transferred to the analytical system, pump *C* was cooled and shut-offs 6 and 7 were opened. The sample then occupied the whole of the analytical system between shut-offs 5 and 8.

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[1] Langmuir: *Jnl.* Amer. Chem. Soc. (1913) **35,** 105.

Liquid air was first applied to the trap and the decrease in pressure measured the CO_2 present in the sample. After this was measured, the gas sample was compressed again into the ignition bulb between 6 and 7. Pure oxygen of known amount was admitted to the system through shut-off 8 with liquid air on the trap. The gas sample was released into the system and the new pressure read after equilibrium was attained.

The sample and oxygen were compressed into the ignition bulb containing a 5-mil filament of pure platinum. This was heated to a dull red for 10 min. Previous work with known amounts of H_2, CO and O_2, in the analytical system, had shown that this time sufficed for the reaction of

$$CO + \tfrac{1}{2}O_2 = CO_2$$

The oxidation of hydrogen to water was very rapid at this temperature.

At first it was feared that in compressing samples containing oxygen with the small mercury pump, some of the oxygen might react with the mercury vapor and the attendant decrease in pressure give a false indication. This point was tested by circulating pure oxygen, and also various combustible mixtures for ½ hr., with the pump. No change in pressure was found. This is in conflict with the findings of Hibben[2] who dropped mercury through oxygen at low pressures and observed a decrease in pressure.

The sample of unknown gas, after undergoing combustion, was released into the system with CO_2 snow ether on the trap. The decrease in pressure, if any, was due to the hydrogen and oxygen which had reacted, plus the oxygen which had combined with carbon monoxide. The contraction which followed when the liquid air was placed on the trap measured the carbon dioxide present. When the amount of carbon dioxide originally found was subtracted, the rest of the contraction represented carbon monoxide originally present, which was oxidized to carbon dioxide. The amounts of gas accounted for by this procedure were then subtracted from the original volume of sample, and the residual considered to be nitrogen. Preliminary work had shown that no oxygen was present in the gases from molybdenum.

Hydrogen was not a common constituent. Large quantities of hydrogen were collected when the bake-out was known to be poor, due probably to water vapor from the glass surfaces reacting with the hot molybdenum. There was also a possibility that some hydrogen came from the sample during the 800° bake-out.

Detailed Calculation

A typical calculation is given below. The pressure readings were made on Hale-Pirani and McLeod gages, but only the latter readings were used as a basis for calculations. It is not necessary to calculate the pressure readings to absolute amounts to determine percentage composition.

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[2] Hibben: *Jnl.* Phys. Chem. (1930) **34,** 1397.

DATA SHEET

McLeod-gage Reading, Microns	Conditions
1.58	Carbon dioxide snow ether on trap.
1.48	Liquid air on trap.
3.45	Oxygen admitted; liquid air on trap.
3.53	Carbon dioxide snow ether on trap.
3.33	After compression and ignition; carbon dioxide snow ether on trap.
3.04	Liquid air on trap.

CALCULATION

Microns	
(a) $1.58 - 1.48 = 0.10$	Carbon dioxide.
$\frac{0.10}{1.58} \times 100 = 6.3$ per cent	Carbon dioxide.
(b) $3.45 - 1.48 = 1.97$	Oxygen admitted.
(c) $3.45 + 0.10 = 3.55$	Pressure before ignition, when carbon dioxide snow ether is on trap.
(d) $3.55 - 3.33 = 0.22$	Contraction on ignition.
(e) $3.33 - 3.04 = 0.29$	Total carbon dioxide condensed by liquid air.
(f) $0.29 - 0.10 = 0.19$	Carbon dioxide which resulted from the carbon monoxide originally present.
$\frac{0.19}{1.58} \times 100 = 12.0$ per cent	Carbon monoxide.

(g) This carbon monoxide, in burning, consumed one-half its volume of oxygen $= 0.10$ microns oxygen.

(h) $0.22 - 0.10 = 0.12$ microns	Residual part of contraction (d) due to hydrogen and oxygen.
(i) $0.12 \times \frac{2}{3} = 0.08$ microns	Portion of contraction due to hydrogen.

$$\frac{0.08}{1.58} \times 100 = 5.1 \text{ per cent hydrogen}$$

(j) The portion of the 1.58 accounted for is now:

$$\underset{\text{carbon dioxide}}{0.10} + \underset{\text{carbon monoxide}}{0.19} + \underset{\text{hydrogen}}{0.08} = 0.37 \text{ microns}$$

(k) The residual noncombustible gas, not condensible by liquid air, is considered to be nitrogen.

$$1.58 - 0.37 = 1.21 \text{ microns}$$

$$\frac{1.21}{1.58} \times 100 = 76.6 \text{ per cent nitrogen}$$

Greater accuracy can be attained when the composition of the gas is known approximately and the amount of oxygen added is only slightly in excess of that necessary.

Temperature Measurement

Temperature measurement was made by means of a Leeds & Northrup optical pyrometer of the disappearing-filament type. It was calibrated against a standard ribbon filament lamp. The pyrometer is scaled to read the correct temperature for a black-body emitter. An incandescent metal surface, as in our experiments, emits less radiation than a black body at the same temperature. The brightness temperature which we measure with the optical pyrometer is thus lower than the true temperature of the sample.

The relationship between true and brightness temperature is discussed by Forsythe and Worthing.[3]

For light of a given wave length λ, the relationship is

$$\frac{1}{T} - \frac{1}{S} = \frac{2.303 \log_{10} e}{C_2}$$

where

T = temperature, deg. K.
S = brightness temperature, deg. K.
λ = wave length of light used in the measurement: here $\lambda = 0.665$ microns.
e = emissivity of the substance for this wave length.
C_2 = Wien's constant = 14330 micron degrees.

A perfect black body has an emissivity equal to unity, and the brightness and true temperature are equal. Other materials have lower emissivity. Worthing[4] gives $e = 0.352$ for the emissivity of molybdenum at 2000°. The data there given are for seasoned molybdenum filaments.

In the present investigation, the emissivity for fresh molybdenum surfaces which had been cleaned by caustic dipping, as described later, was unknown. Following a suggestion by Dr. Dushman, it was determined by drilling a 50-mil hole 200 mils deep into molybdenum samples 250 mils thick. The brightness temperature of the hole and surrounding surface were then measured, the hole constituting a black body. The emissivity thus found was 0.40 at 2033° K., compared to Worthing's value of 0.35, indicating that the rougher molybdenum surfaces of our samples were nearer black-body conditions. The difference between brightness temperature and true temperature of the molybdenum amounted to 160°, at 2033° K. = 1760° C. true temperature = 1600° C. brightness temperature.

The standard temperature used in most of the experiments, 1760° C. (1600° C. brightness temperature), was chosen because below it completion of gas evolution was too slow to be convenient, and above this temperature appreciable evaporation of molybdenum took place. This resulted in a clean-up of some of the gas given off, and it was found that runs at 100° above the chosen temperature gave less gas.

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[3] Forsythe and Worthing: *Astrophys. Jnl.* (1925) **61**, 146.
[4] Int. Crit. Tables V, 243.

PREPARATION OF SAMPLE

The sheet molybdenum was cut with a hacksaw into rough shape. A $\frac{7}{16}$-in. hole was drilled in the center, and a hole for the 100-mil wire for support of the sample. The outside was then turned off on a lathe, so a ring resulted, with the oxide, if originally present, on the faces.

The sample, on a clean molybdenum rod, was dipped into a bath of molten caustic with about 3 per cent nitrite in it at 450° C. About 30 sec. cleaned off the oxide. The ring was then dipped successively into hot water, 10 per cent hydrochloric acid solution, cold water, washed thoroughly in distilled water, dipped into grain alcohol and dried in a stream of air. Care was taken to avoid touching the sample at any stage of cleaning. It was handled with tweezers and kept wrapped in condenser paper.

Some samples, as noted, were further treated by electrolyzing in concentrated sulfuric acid, with a strip of molybdenum sheet as cathode and the sample as anode. The appearance of the electrolyzed samples was bright and shiny, compared to the dull gray of the caustic-dipped samples. The caustic-dipped samples showed clearly the fibrous structure of the metal.

NATURE OF GAS EVOLVED AT VARIOUS TEMPERATURES

Table 1 and Figs. 3 and 4 show the results obtained as a sample is heated to successively higher temperatures and the gas evolved at each stage is collected and analyzed.

In these experiments the high temperature (800° to 1000° C.) bake-out oven was not put on the quartz. It received the 450° bake-out with the rest of the system. When the evolution of gas from the sample was at an end, or at a steady rate, for a given temperature, the sample was pumped over to the analytical system, and the rate checked again at low pressures in the collection system, to be sure of the rate, or of the complete cessation of gas evolution.

These experiments and the data summarized in Fig. 4 are of especial interest in showing the relative ease with which the constituent gases come off.

Hydrogen comes off most readily, at the lower temperatures, as Alleman and Darlington[5] found with ferrous alloys. The amount of this is relatively small.

The next gas to appear in quantity is carbon monoxide, which comes off readily at 1000° and lower. It persists, in small amounts, to the higher temperatures.

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[5] Alleman and Darlington: *Jnl.* Frank. Inst. (Feb.-Apr., 1918).

TABLE 1.—*Gas Evolved in Stages and at Single Temperatures*

Brightness Temperature, Deg. C.	True Temperature, Deg. C.	Gas (NTP), Cu. Mm.	Gas Composition, Per Cent				Amounts of Gas, Cu. Mm.			
			N_2	CO	CO_2	H_2	N_2	CO	CO_2	H_2
EXPERIMENT 2. GAS IN STAGES FROM 70-MIL, 4.9-GRAM SAMPLE, CAUSTIC-DIPPED										
740	790	4.00	4	75	21		0.16	3.00	0.84	
940	1010	1.65	16	42	15	27	0.26	0.69	0.25	0.45
1120	1210	9.70	81	15		4	7.85	1.45		0.40
1312	1440	5.23	76	10	6	8	4.00	0.52	0.31	0.40
1600	1760	1.15	45	24	7	24	0.52	0.27	0.09	0.27
Total.....		wtd. 21.73 ave.	59	27	7	7	12.79	5.93	1.49	1.52
EXPERIMENT 296. GAS AT SINGLE TEMPERATURE FROM 70-MIL, 4.9-GRAM SAMPLE, CAUSTIC-DIPPED										
1600	1760	24.8	58	30	6	6	14.4	7.4	1.5	1.5
EXPERIMENT 12 (FIG. 3). GAS IN STAGES FROM 72-MIL, 5.3-GRAM SAMPLE, CAUSTIC-DIPPED										
740	790	5.44	5	66	20	9	0.28	3.58	1.09	0.49
978	1050	3.66	66	30	4		2.41	1.10	0.15	
1115	1210	9.00	95	5			8.55	0.45		
1320	1450	9.40	90	10			8.46	0.94		
1500	1650	1.20	90	10			1.08	0.12		
1600	1760	0.22					(0.22)			
Total.....		wtd. 28.92 ave.	73	21	4	2	21.0	6.19	1.24	0.49
EXPERIMENT 34. GAS AT SINGLE TEMPERATURE FROM 72-MIL, 5.3-GRAM SAMPLE, CAUSTIC-DIPPED										
1600	1760	20.0	94		6		18.8		1.2	

Nitrogen is more difficult to remove and requires a temperature of 1200° and up before it comes off. It is of interest to note that molybdenum nitride may exist as shown by Langmuir.[6]

EFFECT OF TREATMENT AND SOURCE ON GASES FROM MOLYBDENUM

In the light of the previous experiments it was decided to carry out all subsequent experiments at 1760° C. This seemed to be the optimum temperature; at lower temperatures the time for complete degassing was excessive and at higher temperatures evaporating molybdenum cleaned up some of the gas evolved. Samples degassed completely at 1760° C. gave off no further gas on being taken to higher temperatures.

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[6] Langmuir: *Jnl.* Amer. Chem. Soc. (1913) **35**, 105, 931. (1915) **37**, 417, 1139. See Mellor: Treatise on Inorganic Chemistry, **V**, 128.

Table 2 gives the amounts and composition of the gases obtained from the samples of molybdenum from various sources. Figs. 5 and 6 illustrate the rate at which the gases are evolved and together with the tables present the results obtained. From these data it is evident that samples from all the different sources give about the same amount of gas and require about the same time for complete degassing. No correlation could be found between different methods of manufacture, such as amount of working, and the gas content.

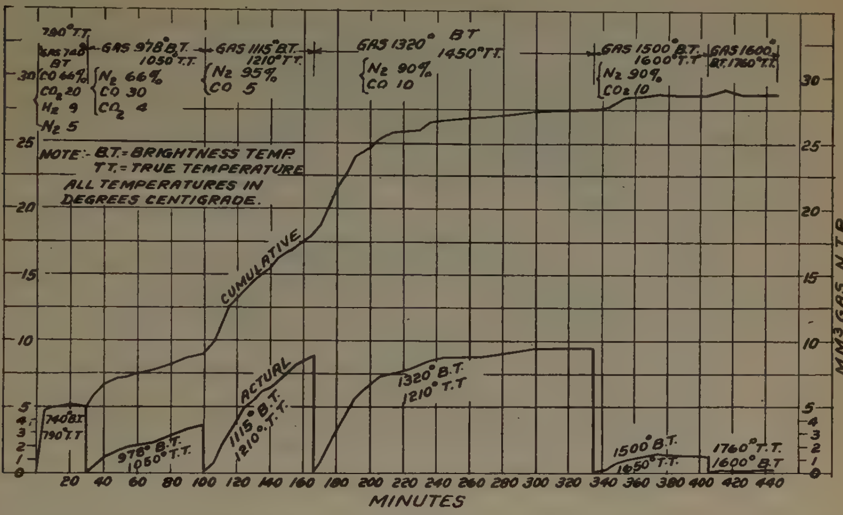

Fig. 3.—Gas evolved from molbydenum. 72-mil, 5.3-gram sample, caustic-dipped.

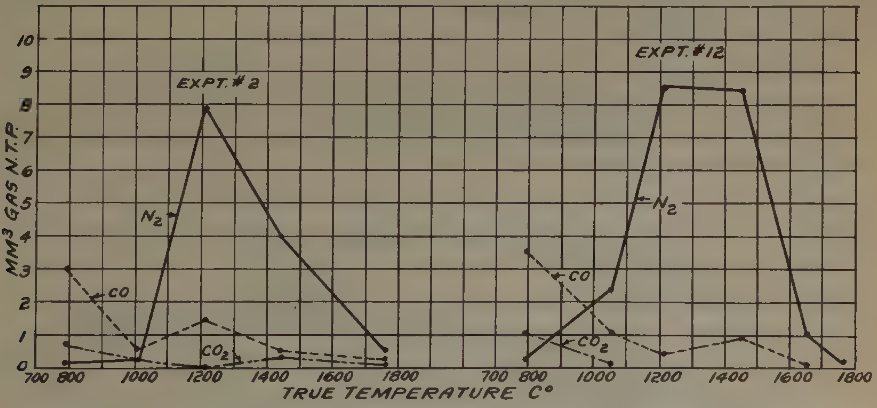

Fig. 4.—Amount of gases given off at various temperatures.
Molybdenum ring, 7⁄16-in. inside diameter, 7⁄8-in. outside diameter and 0.07 in. thick.

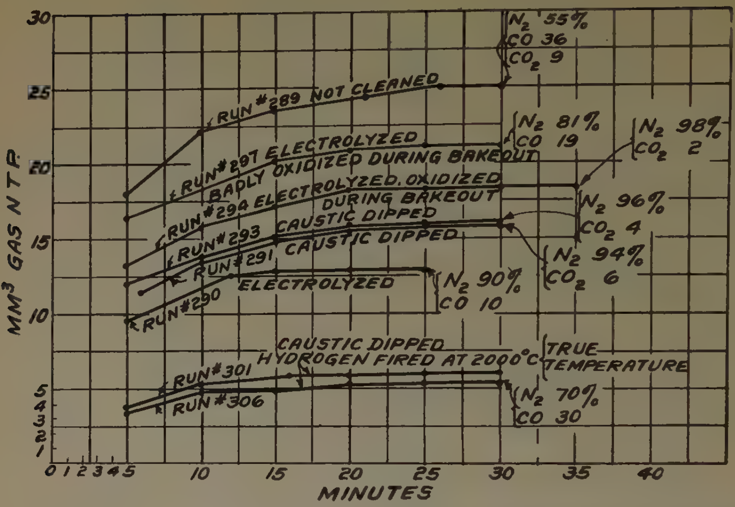

FIG. 5.—GAS EVOLVED FROM MOLYBDENUM. 70-MIL, 5.1-GRAM SAMPLE DEGASSED AT 1760° C. TRUE TEMPERATURE.

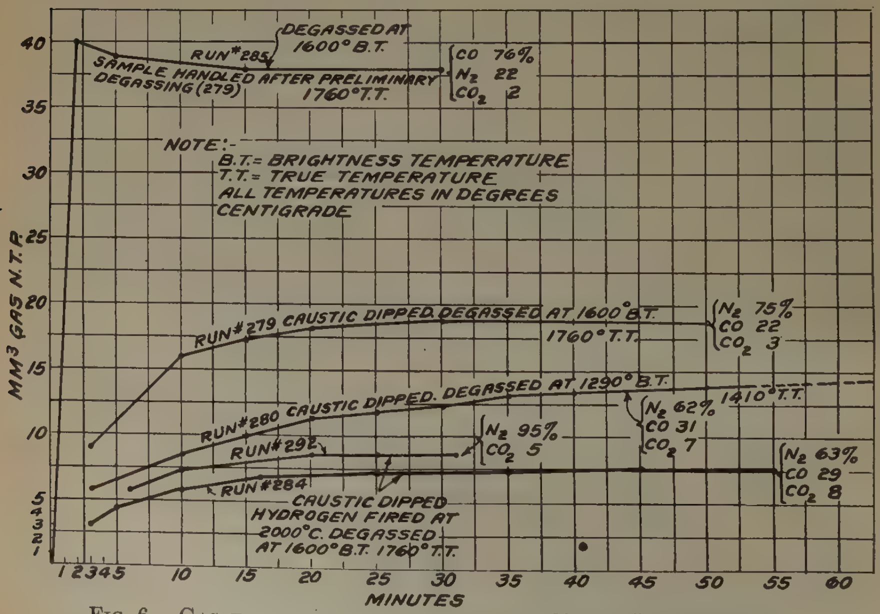

FIG. 6.—GAS EVOLVED FROM MOLYBDENUM. 69-MIL, 5-GRAM SAMPLE.

TABLE 2.—*Molybdenum Samples Degassed at a Single Temperature*

Stock No.	Expt. No.	Cleaning			Thickness, Mils	Time for Degassing, Min.	Gas Composition, Per Cent				Weight of Sample, Grams	Amount of Gas, Cu. Mm. (NTP)				
		NaOH Dip	Electro-lyzed	Hydrogen-fired			N_2	CO	CO_2	H_2		N_2	CO	CO_2	H_2	Total
1760° C. TRUE TEMPERATURE																
3	268	*			73	25	88	12			5.1	9.2	1.3			10.5
3	272	*			73	25					5.1					10.7
3	271	*			73	22	93	7			5.1	7.5	0.55			8.05
4	286	*			70	25	95		5		5.0	22.4		1.2		23.6
4	287	*	*		70	25	86	12	2		5.0	17.5	2.5	0.4		20.4
4	288	*		*	70	25					5.0					6.07
4	300	*		*	70	20	81	16	3		5.0	4.3	0.85	0.20		5.35
4	305	*		*	70	25	91	9			5.0	4.4	7.4	1.5	1.5	4.85
5	296	*			70	15	58	30	6	6	4.9	14.4	7.4	1.5	1.5	24.8
5	309	*			70	20					4.9					13.7
7	27	*	unworked		250	115	63	27	5	5	17.9	20.2	8.7	1.6	1.6	32.1
8	31	*	worked		250	120	95		5	11	17.9	16.9		0.9		17.8
10	263[a]				70	70	35	65			5.1	14.0	26.0			40.0
10	274[b]		*		70	20	82	15	3		5.1	15.6	2.9	0.5		19.0
10	302	*		*	70	20	59	36	5		5.1	3.6	2.2	0.27		6.07
10	304	*		*	70	16					5.1					4.37
11	276	*			25	11	78	19	3		1.8	11.4	2.8	0.4		14.6
12	307	*			69	30	68	26	6		5.1	17.3	6.6	1.6		25.5
12	308		*		69	20	95	5			5.1	20.3	1.1			21.4
1	299	*	*		25	5	81		2	17	1.8	11.6		0.3	2.4	14.3
1	298	*	*		25	4	85	4	3	8	1.8	11.1	0.5	0.4	1.1	13.1

Table continued on next page.

TABLE 2.—(*Continued*)

Stock No.	Expt. No.	Cleaning			Thickness, Mils	Time for Degassing, Min.	Gas Composition, Per Cent				Weight by Sample, Grams	Amount of Gas, Cu. Mm. (NTP)				
		NaOH Dip	Electro-lyzed	Hydrogen-fired			N_2	CO	CO_2	H_2		N_2	CO	CO_2	H_2	Total
2	289[c]				70	26	55	36	9		5.1	13.8	9.0	2.2		25.0
2	297[d]		*		70	25	81	19			5.1	17.1	4.0			21.1
2	294[e]		*		70	30	98		2		5.1	18.0		0.4		18.4
2	290[f]		*		70	15	90	10			5.1	11.5	1.3			12.8
2	293	*			70	25	96		4		5.1	15.4		0.6		16.0
2	291	*			70	25	94		6		5.1	14.8		1.0		15.8
2	301	*		*	70	25					5.1					6.05
2	306	*		*	70	25	70	30			5.1	3.7	1.55			5.25
9	285[g]				69	2	22	76	2		5	8.8	30.4	0.8		40.0
9	279	*			69	30	75	22	3		5	14.1	4.1	0.6		18.6
9	292	*		*	69	20	95		5		5	8.2		0.4		8.6
9	284	*		*	69	45	63	29	8		5	4.9	2.2	0.6		7.7

[a] Filed clean; washed with benzol.
[b] Oxidized during bake.
[c] Not cleaned. No oxide on sample.
[d] Badly oxidized in bake.
[e] Oxidized in bake.
[f] Not oxidized.
[g] Handled after degassing, then not cleaned.
* Indicates that these received treatment of column heading.

The rate of gas evolution was found to be of the first order and this together with evidence presented later seems to show that the controlling factor in the gas evolution is the diffusion of gas to the surface from within the sample.

EFFECT OF VARIOUS METHODS OF CLEANING

From the tabulations it is evident that methods of preparing the sample give greater differences than appear in samples from various sources. A summary of the effect of various methods of cleaning on gas evolution is given in Table 3, in order of increasing effectiveness. The samples were all 70 mils thick. The first treatment represents the result of one experiment; the others are the average of several.

TABLE 3.—*Effect of Method of Cleaning on Gases Evolved*

Treatment	Time of Degassing, Min.	Amount of Gas, Cu. Mm. (NTP)	Gas Composition, Per Cent		
			N_2	CO	CO_2
Filed clean and washed in benzol...	70	40	35	65	
Caustic-dipped.....................	24	22.5	79.0	16.5	4.5
Electrolyzed conc. H_2SO_4..........	20	17.1	88.5	10.5	1.0

The decreasing amounts of carbon monoxide in the series in Table 3 is interpreted as more complete removal of surface grease and dirt, but from the curves in Figs. 3 and 4 it is apparent that carbon monoxide continues to come out even at later stages of the degassing, apparently from the body of the metal.

The effect of dirt and grease is shown by experiments 285 and 279 (Table 1 and Fig. 6). A caustic-dipped sample was run in the regular manner, No. 279. It gave off 18.8 cu. mm. of gas, 75 per cent N_2 and 22 per cent CO, and required 30 min. for complete degassing. This same sample was taken out and handled, then put back into the system and a regular bake-out given. Then on degassing (experiment 285) at 1760° C., 40 cu. mm. of gas came off in 2 min. It consisted of nitrogen 22 per cent, carbon monoxide 76 per cent. The rapidity with which this gas comes off can be explained by the fact that it is absorbed only on the surface of the sample.

PERMANENCE OF DEGASSING

One of the most striking things found in this investigation of molybdenum was that a sample once degassed stays degassed, if proper precautions are taken. The most important requirement is to avoid handling the sample, as shown in the preceding section.

If precautions are taken, and the sample handled with tweezers and kept wrapped in condenser paper, the surface contamination is reduced to a minimum, as in experiment 104. A sample was degassed in the Arsem furnace,[7] then in the quartz apparatus. It was taken out, handled only with tweezers and kept wrapped in ½ mil condenser paper for 42 days. On degassing this sample in the regular manner after that length of time, the results shown in Table 4 were obtained.

TABLE 4.—*Experiment No.* 104, *Sample* 70 *Mils Thick*

Gas Evolved, Cu. Mm. (NTP)	True Temp., Deg. C.	Time for Complete Degassing, Min.	Gas Composition, Per Cent		
			N_2	CO	CO_2
1.41	1275	10	15	73	12
.51	1760	10	31	50	19
Total 1.92					

Similar results were obtained for a sample which had been degassed, taken out, caustic-dipped, washed in water and alcohol, and degassed again. This sample weighed 4.9415 g. before caustic dip, 4.8900 g. after caustic dip; *i. e.*, 0.0515 loss on NaOH dipping, or 1.04 per cent loss. The original sample was 72 mils thick; the edge area makes up 24 per cent of the total surface area. Hence the caustic dip, assuming uniform attack, reduced the 72 mils thickness by $0.76 \times 0.0104 \times 72 = 0.58$ mils. The removal of this thickness of molybdenum had the result shown in Table 5 on the amount of gas at the second degassing. This indicates that the gas has been removed at least to a depth of 0.58 mils. The question of the depth to which degassing has proceeded is discussed in the following section.

TABLE 5.—*Experiment No.* 24

Gas Evolved, Cu. Mm. (NTP)	True Temp., Deg. C.	Time for Degassing, Min.	Gas Composition, Per Cent	
			N_2	CO
1.3	1760	3	87	13

Two other experiments may be cited in which the samples were not taken from the apparatus, but exposed to wet air after degassing and then degassed the second time. Small amounts of gas were obtained, corresponding closely to a monomolecular layer. The sample of experiment 103 had stood in contact with the atmosphere for 15 hr., experiment 110 for 40 hr. The 0.25 cu. mm. of gas from experiment 110 was 57 per cent N_2, 43 per cent CO. This, incidentally, represents the smallest amount of gas that was analyzed.

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[7] An Arsem furnace is a vacuum furnace heated by a carbon resistor.

TABLE 6.—*Experiments on Samples Exposed to Wet Air and Degassed a Second Time*[a]

Experiment No.	Gas Evolved, Cu. Mm. (NTP)	True Temp. Deg. C.	Time for Complete Degassing, Min.
103	0.07	1060	5
	0.24	1760	5
	0.31		
110	0.15	1260	5
	0.10	1760	5
	0.25		

[a] Regular bake-out procedure, glass at 450° C., quartz and sample at 800° C.

In Langmuir's paper on the absorption of gases by glass, mica and platinum,[8] he shows that for an average molecular diameter of 3×10^{-8} cm., a monomolecular layer over 1 sq. cm. of surface corresponds to 0.04 cu. mm. gas (NTP). The samples of molybdenum used in this investigation had a total surface area, (from the gross dimensions) of 7.65 sq. cm. which should give 0.306 cu. mm. of gas for a monomolecular

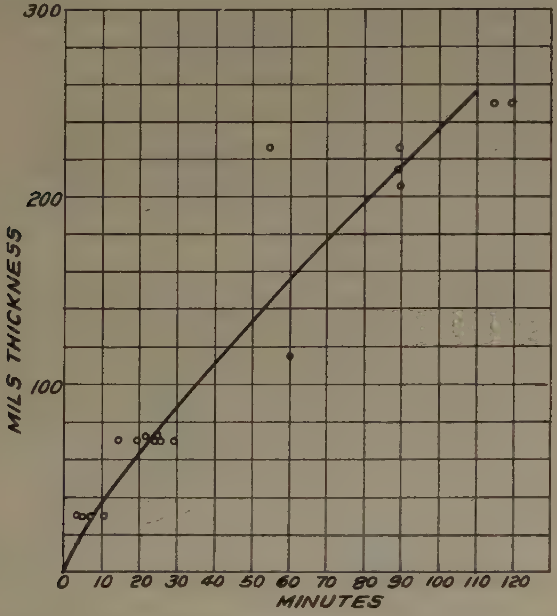

FIG. 7.—TIME OF COMPLETE DEGASSING FOR SAMPLES OF VARIOUS THICKNESSES. Molybdenum ring 7/16-in. inside diameter, 7/8-in. outside diameter, 1760° true temperature.

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[8] Langmuir: *Jnl.* Amer. Chem. Soc. (1918) **40,** 1361.

TABLE 7.—*Arsem Furnace Experiments*

Molybdenum Samples 0.070 in. Thick

Experiment No.	Furnace Conditions				Degassing		Gas Composition, Per Cent			Total Amount of Gas, Cu. Mm.
	Time of Firing, Hr.	Temperature, Deg. C.	Vacuum		Temperature, Deg. C.	Time for Complete Degassing, Min.	N_2	CO	CO_2	
			McLeod, Microns	Hale-Pirani, Microns						
39	1	1625	125	100	1760	15	58	37	5	5.8
40	2	1625	50	80	1760	15	66	34		3.65
65	1	1780	100	100	1760	20	50	43	7	8.93
66	½	1780	150	100	1760	15	71	24	5	3.60
70	1	1770	75	100	1760	5	10	84	6	2.97[a]
77	2	1780	50	90	1760	10		90	10	4.23
								Ave.		4.86

[a] Best.

layer. This agrees with the values found above of 0.25 and 0.31 cu. mm. within the limits of accuracy for the method.

A number of experiments were made to determine whether a high vacuum was necessary to degas molybdenum. Samples were heated in a carbon tube vacuum furnace, a tungsten tube vacuum furnace and in hydrogen of various degrees of purity. An analysis was made of the atmosphere of the tungsten furnace when it was operating at 2000° C. and a vacuum of 6 microns, as follows: H_2, 86.5 per cent; N_2, 8 per cent; CO, 3.5 per cent; CO_2, 2 per cent.

Degassing in Arsem Vacuum Furnace.—Samples of molybdenum, 73 mils thick, caustic-dipped, were first degassed in an Arsem furnace, taken out, using care in handling, and degassed again in the quartz apparatus. The results are given in Table 7.

Tungsten Vacuum Furnace.—In order to obtain better vacuum than is possible in an Arsem furnace, an iron-jacketed vacuum furnace with a tungsten heater was set up. The heating unit consisted of a wire cage, of about 75 pieces of 80-mil tungsten wire, on supports of copper brazed in iron. The supports were water-cooled. The best vacuum obtained in this furnace was 5 microns measured on a Hale-Pirani gage while the furnace was at 1950° C. and 2 microns at 1800° C. (Table 8.)

Hydrogen Firing.—It was found that samples fired in a tube hydrogen furnace at atmospheric pressure and 2000° C. gave off less gas on subsequent degassing than was present in unfired samples. The degassing time was not very different. (Table 9.)

It is noteworthy that hydrogen was not found in the gas from these hydrogen-fired samples. The explanation is to be found in the ease with which hydrogen comes off, so that undoubtedly it was given off during the 800° bake-out of the quartz and sample.

Experiments were then performed with purified hydrogen. The line hydrogen was passed through a liquid-air trap over heated platinized asbestos and through a second liquid-air trap. It was then led into the bottom of the quartz container and past the sample, at atmospheric pressure and a rate of about 4 c.c. per minute. The sample was kept heated by high frequency during this time. The quartz lead in tube was then sealed off, system evacuated and regular bake-out and degassing in vacuo followed.

In experiment 153 a sample was fired at 1600° C. for 1 hr. in purified line hydrogen at atmospheric pressure. On degassing it gave off 2.38 cu. mm. of gas in 25 min., the gas being 89 per cent N_2 and 11 per cent CO. In experiment 156, another sample was fired in the same way at 1740° C. It evolved 2.0 cu. mm. of gas, 16 per cent N_2, 69 per cent CO and 15 per cent CO_2.

Attempts were then made to obtain still purer hydrogen. A small, thin-walled palladium tube was attached to the bottom of the quartz

TABLE 8.—*Tungsten Furnace Experiments*
Molybdenum Samples 0.070 in. Thick

Experiment No.	Furnace Conditions					Quartz Apparatus Degassing					
	Time of Degassing, Hr.	Temperature Deg. C.	Vacuum			Temperature Deg. C.	Time for Complete Degassing, Min.	Gas Composition, Per Cent			Total Amount of Gas, Cu. Mm.
			McLeod, μ	Hale-Pirani, μ	Ionization Gage (Liquid Air On), μ			N_2	CO	CO_2	
75	1	1800		10	1.5	1760	20				6.44
76	½	1800	1.5	10		1760	5	15	74	11	2.77
79	1	1800		5	0.4	1150	5	3	88	9	2.38
						1760	15	13	76	11	1.70
											4.08
96	1	1800	3	8	0.8	1760	40	17	79	4	8.0
97	½	1800	2.5	6	0.6	1250	10		63	37	1.14
						1760	30		85	15	2.06
											3.20
99	2	1800	1.5	4	0.3	1300	5	23	65	12	0.68
						1760	15		72	18	1.60
											2.28[a]
120	½	1950	2	8		1280	20	60	40		0.92
	10	1650	1.4	5		1760	25	70	30		1.60
											2.52
125	1	1980	2	6		1300	20	21	67	12	1.5
						1760	20	30	59	11	2.5
											4.0
										Ave.	4.16

[a] Best.

TABLE 9.—*Gas from Hydrogen-fired Samples*

Hydrogen Fired in Tube Furnace at 2000° C., ½ hr. to 1 hr. Degassed at 1760° C.

Experiment No.	Degassing Time, Min.	Amount of Gas, Cu. Mm (NTP)	Gas Composition, Per Cent		
			N_2	CO	CO_2
304	16	4.37			
305	25	4.85	91	9	
306	25	5.25	70	30	
300	20	5.35	81	16	3
301	25	6.05			
288	25	6.07			
302	20	6.07	59	36	5
284	45	7.70	63	29	8
292	20	8.60	95		5
Average....	25	6.07			

container by a graded seal. Surrounding this was a quartz tube, which had no connection to the quartz sample container, but served to conduct hydrogen past the palladium tube. A small tube furnace surrounded it and was kept at 1100° C. At this temperature, hydrogen was able to diffuse through and past the molybdenum sample, which was heated by high frequency. The pressure inside the system was kept at two-thirds of an atmosphere, to obtain a faster stream of hydrogen. In the best experiment, No. 149, the gas evolved is of the order of a monomolecular layer.

TABLE 10.—*Heating in Hydrogen Diffused through Palladium*

Heating in H_2				Degassing Sample in Quartz				
Experiment No.	Pressure, Cm.	Temperature, Deg. C.	Time, Hr.	Temperature, Deg. C.	Amount of Gas, Cu. Mm.	Gas Composition, Per Cent		
						N_2	CO	CO_2
138	50	1600	1	1070	0.32			
				1760	1.00	75	25	
				Total	1.32			
140	50	1740	1	1180	0.68	61	39	
				1760	0.46	60	36	4
				Total	1.14			
149	50	1740	1	1760	0.36	73	27	

Summary of Five Methods.—The five methods just discussed are summarized in Table 11. The "percentage of total gas removed," was calculated, taking 22.5 cu. mm. as the normal amount in a caustic-dipped 70-mil sample. It is thus apparent that the important factor in degassing molybdenum is an atmosphere free from nitrogen, carbon dioxide and carbon monoxide.

TABLE 11.—*Effect of Treatment of Molybdenum on Gas Content*

Method	Gas Left in Molybdenum, Cu. Mm.		Average Percentage, Total of Gas Removed
	Average	Lowest Value	
1. Hydrogen firing, tube furnace, 1 atm.	6.07	4.37	72.7
2. Arsem vacuum furnace	4.86	2.97	78.1
3. Tungsten vacuum furnace	4.16	2.28	81.3
4. Purified line hydrogen, 1 atm.	2.19	2.00	91.2
5. Line hydrogen diffused through heated palladium, at 2/3 atm.	0.94	0.36	95.8

DEGREE OF VOLUME DEGASSING

The preceding experiments have suggested that the gas comes from the interior of the sample. This idea is supported when the time required

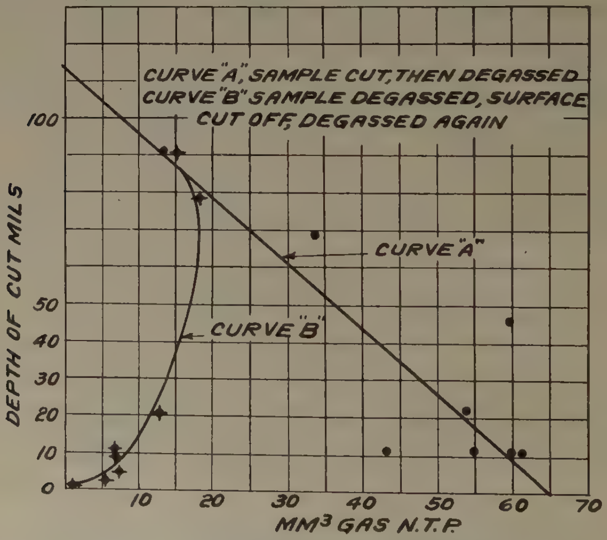

FIG. 8.—GAS EVOLVED AT VARIOUS DEPTHS.

Molybdenum ring 7/16-in. inside diameter, 7/8-in. outside diameter. Original 227 mils thick. 1760° C. true temperature.

for complete degassing is compared with the thickness of the sample (Fig. 7). The data in Fig. 7 are all for the standard sized ring, degassed at 1760° C. The fact that a volume and not a surface relationship is involved is also indicated by the relative change in thickness, surface area and degassing time in going from a 25-mil to a 250-mil sample.

TABLE 12.—*Degree of Volume Degassing*

Experiment No.	Orig. Thickness, Mils	Cut to, Mils	Depth of Cut, Mils	Degassing Temperature, Deg. C.	Degassing Time, Min.	Gas Composition, Per Cent			Amount of Gas, Cu. Mm. (NTP)			Total
						N_2	CO	CO_2	N_2	CO	CO_2	
SAMPLES CUT, THEN DEGASSED												
83	250	227	11	1760	90	69	27	4	42.2	16.5	2.2	61.1
71	250	227	11	1760	55							59.8
81	250	227	11	1170	50	31	69		9.4	20.8		30.2
				1760	62	46	54		6.1	7.1		13.2
												43.4
68	250	206	22	1760	90	55	43	2	29.7	22.8	1.1	53.6
61	250	161	45	1760	40	77	19	4	46.0	11.4	2.4	59.8
88	250	115	68	1760	60	25	71	4	8.4	23.8	1.6	33.8
44	250	70	90	1760	25	63	30	7	8.4	4.0	1.0	13.4
SAMPLES DEGASSED, CUT, DEGASSED AGAIN												
20	71	66	2.5	1760	5	57	30	13	2.9	1.5	0.7	5.1
91	161	151	5	1760	15	32	68		2.4	5.0		7.4
93	227	209	9	1760	5	36	64		2.5	4.4		6.9
22	66	41	10	1760	5	63	30	7	4.2	2.0	0.4	6.6
95	227	186	20	1760	10	13	82	5	1.6	10.3	0.7	12.6
90	227	70	79	1760	16	54	43	3	9.9	7.9	0.6	18.4
43	250	70	90	1760	20	28	72		4.2	10.9		15.1

These considerations led to a series of experiments in which a set of samples was made from 250-mil stock, cut down on a lathe to various thicknesses, taking equal cuts from each side. The samples were then degassed by standard procedure. Another set of samples of molybdenum was first degassed, the surface cut down to various depths, and the samples degassed again. All were subjected to identical conditions as far as possible. All were from one stock piece of molybdenum. None were caustic-dipped to avoid heating, but the scale on the original 250-mil piece was cut off on the lathe, bringing it to 227 mils. The samples were washed after cutting, in benzol then in alcohol and dried without touching.

The results are given in Table 12 and in Fig. 8. These indicate that the degassing has reached about 90 mils = 0.090 in. into the sample, for at that point the amount of gas given off was the same whether or not the sample had a preliminary degassing.

The amount of gas present in the undegassed samples is proportional to the thickness of the sample, which is positive proof that we are dealing with gas inside in the metal.

Degassing of Tungsten

Several tungsten rings were degassed in a high vacuum at temperatures ranging from 1400° to 2600° C. (Table 13.)

Table 13.—*Degassing of Tungsten*

Total Gas Evolved, Cu. Mm. (NTP)	Gas per Gram of Tungsten, Cu. Mm.	Percentage of Gas by Weight	Thickness, Mils.	Gas per Cu. Cm. of Tungsten, Cu. Cm.
5.94	0.41	0.000051	83	0.0077
3.33	0.23	0.000029	83	0.0042

Amounts of Gas Evolved from 14.5-Gram Sample

Experiment No.	Temperature, Deg. C.	Time of Heating, Min.	Composition of Gas, Cu. Mm.				Total Gas, Cu. Mm.
			H_2	CO	CO_2	N_2	
169	1410	15	0.07	0.36	0.05	0.55	1.04
	1740	50		0.61	0.36	1.80	2.78
	2140	35		0.91	0.03	0.65	1.59
	2490	25		0.53			0.53
Total.....			0.07	2.41	0.44	3.0	5.94
172	1440	20	0.09	0.46		0.49	1.04
	1740	50		0.13		1.31	1.44
	2130	25		0.29		0.44	0.73
	2430	20		0.12			0.12
	2610	15					0.02
Total.....			0.09	1.00		2.24	3.33

To degas tungsten at a rate comparable to that obtained with molybdenum at 1800° C. it is necessary to heat to 2300° C. It is interesting to note in experiment 172 that further heating at 2610° C. produced no further gas evolution after degassing had been completed at 2430° C. The amount of gas obtained from a sample of tungsten ranges from 15 to 25 per cent of that obtained from a similar sample of molybdenum.

DEGASSING OF NICKEL

At 1030° C., nickel has the same vapor pressure as molybdenum at 1760° C. (approx. 0.003 microns) and this is the highest temperature at which nickel can be maintained for a long period in a high vacuum without noticeable evaporation.

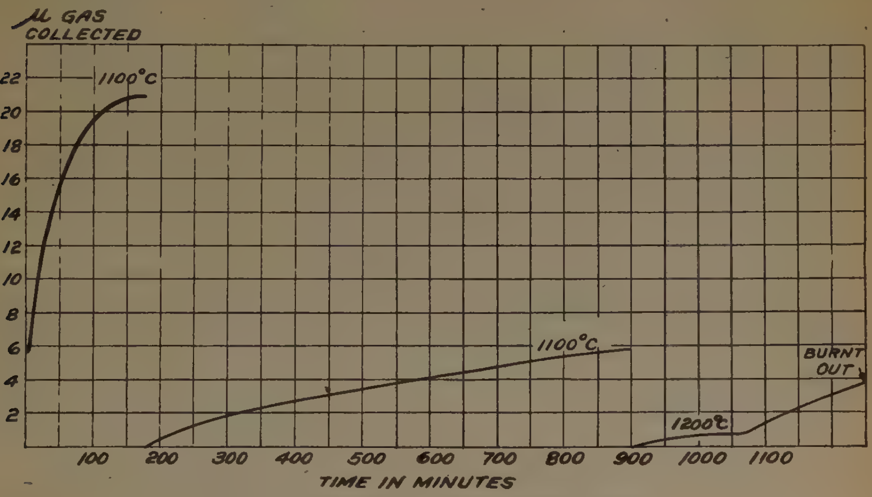

FIG. 9.—DEGASSING OF ELECTROLYTIC NICKEL.
1μ = 2.8 cu. mm. Sample weight 4.5 grams.

The first sample examined was taken from a nickel ingot which had been made from electrolytic nickel by vacuum-melting in an alumina crucible. The ring had an internal diameter of $\frac{7}{16}$ in. and an external diameter of $\frac{7}{8}$ in. and was 250 mils thick. In 5 min. at 950° C. 10 microns of gas were evolved and in a subsequent 45 min., 0.6 microns. The next sample was made from electrolytic nickel and was 71 mils thick. (Table 14.) The sample in the last experiment evaporated more rapidly on one side than the other and finally melted at this spot and open circuited the ring.

DEGASSING OF CARBON

These experiments deal with the degassing of tungar anodes, which are made from Acheson graphite and are $\frac{23}{32}$-in. dia. and $\frac{1}{4}$ in. thick. The samples were all given a preliminary firing in a hydrogen furnace at 1500° C. and subsequently heated in an Arsem vacuum furnace at

TABLE 14.—*Degassing of Nickel*

Temperature, Deg. C.	Time, Min.	Amount of Gas, Cu. Mm.				
		H_2	CO	CO_2	N_2	Total
RING 250 MILS THICK (16 GRAMS)						
950	5	3.7	18.3	4.2	2.0	28.2
	45					1.7
1050	35	3.1	4.8			2.8 no visible distillation
1170	20					2.3 distillation
1090	400		8.4		1.0	9.4
RING 71 MILS THICK (4.5 GRAMS)						
1100	177	1.1	45.4	5.9	6.5	59.0
	730		14.2	1.1	1.0	16.3
1200	240	1.6	8.8	0.5	0.7	11.7

1800° C. Some of the samples were again fired in hydrogen in the degassing apparatus before degassing in an attempt to remove absorbed oxygen.

TABLE 15.—*Degassing of Carbon* (6.2 *Grams*)

Experiment No.	Apparatus Firing					Temperature, Deg. C.	Gas Evolved, Cu. Mm.				
	Impure H_2	Pure H_2	Press.	Temp., Deg. C.	Time, Hr.		Total	H_2	CO	CO_2	N_2
206	*					1680	8.0	3.2	4.1		0.7
						2090	3.1		0.7	0.1	2.3
203	*					1640	18.4	11.2	6.1	0.6	0.6
						2100	3.7		1.3	0.1	2.4
273	*	*	50μ	1000	1	1330	26.8	13.9	11.8	1.1	
						1640	3.7	1.1	1.8	0.2	0.6
						1950	3.1	0.3	0.4	0.1	2.2
						2175	1.6		0.1	0.1	1.4
256	*	*	40μ	1000	1	1020	11.3	8.4	1.7	0.5	0.8
						1230	20.2	12.9	5.7		2.4
						1330	13.5	7.5	3.5		2.3
						1470	2.3	1.0	0.4		0.9
						1640	2.9	1.5	0.2		1.2
						1950	2.0	0.7	0.5		2.8
						2160	2.0				
266	*	*	3 mm.	1000	1	1020	33.2	21.2	3.3	4.0	4.6
						1330	23.5	16.2	6.6	0.7	
						1640	14.1	11.8	0.6		1.7
						1950	2.0		0.2		1.8
						2140	1.7		0.2		1.5
197	previously degassed and exposed to air before degassing the second time.					980	1.2		0.9		0.3
						1710	1.8	0.6	1.2		
						2130	6.1	3.0	2.0	0.2	0.9

* Denotes treatment in column heading.

At 2150° C. it is possible to degas graphite so that subsequent heating at a higher temperature gives no further gas. It is very interesting to observe that the gas evolved in the range 1700° to 2200° C. is predominantly nitrogen. A piece of graphite which has been degassed completely on subsequent exposure to air absorbs oxygen and some of this is so firmly bound that it is only desorbed as carbon monoxide on subsequent heating to 2150° C.

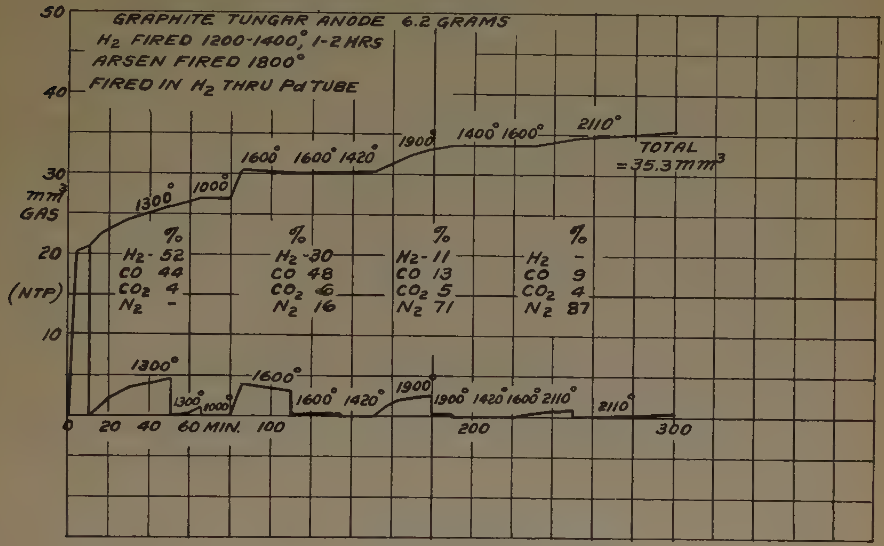

FIG. 10.—DEGASSING OF GRAPHITE.

ABSORPTION OF NITROGEN AND CARBON MONOXIDE BY MOLYBDENUM AND TUNGSTEN

A degassed sample of molybdenum was heated in the air by means of atomic hydrogen flame, which melted the edge of a sample entirely around the circumference, but left it still in the form of a ring. This was then caustic-dipped and the regular degassing procedure applied. The sample then evolved 108.8 cu. mm. of gas at 1760° C. This gas was 96 per cent N_2 and 4 per cent CO_2. In the first 5 min. of heating in vacuo, 92 cu. mm. came off, and an hour longer was required for complete degassing.

In order to study more closely the taking up of gases by molybdenum and tungsten at high temperatures, a new series of experiments was performed. Degassed samples, 70 mils thick, were heated in the quartz chamber by high frequency in dry nitrogen and carbon monoxide, varying temperature, time of heating and pressure of the gas. The system was then pumped out, baked out if necessary, and the sample heated again in a very good vacuum, collecting and measuring the gas evolved from it.

For nitrogen it was found that no glow discharge appeared below 15 microns pressure or above 1 cm. pressure. All of these absorption experiments were performed in regions where no glow discharge appeared.

A detailed description of these experiments will be published elsewhere but a brief summary of the results may be of interest here. It has been found that the solubility of nitrogen in both tungsten and molybdenum is proportional to the square root of the nitrogen pressure. The variation of the solubility with temperature is represented by the equation

$$\frac{d \log (C^2/p)}{d(1/T)} = -\frac{\Delta H}{4.58}$$

where C is the solubility and p the nitrogen pressure. ΔH is the heat absorbed from the surroundings when 1 gram-mol of nitrogen is dissolved.

$$\text{For tungsten} \quad \Delta H = 74{,}700$$

$$\text{molybdenum} \quad \Delta H = 38{,}500$$

The solubility increases rapidly with increasing temperature.

The desorption of nitrogen from tungsten and molybdenum is a diffusion process and hence must obey Fick's law of diffusion

$$\frac{1}{K}\frac{dc}{dt} = \frac{d^2c}{dx^2}$$

This equation on integration shows that

$$\log \frac{a - x}{a} \propto Kt$$

and also that

$$\log \frac{dy}{dt} \propto Kt$$

If the logarithm of the rate of gas evolution at any fixed temperature is plotted as a function of time a ~~straight line is~~ obtained. The variation of the slope of this line as a function of temperature is determined by the variation of the diffusion constant with temperature.

$$\log K = \frac{A}{4.58T} + B.$$

$$\text{For tungsten} \quad A = -50{,}500 \text{ cal.}$$

$$\text{molybdenum} \quad A = -26{,}600 \text{ cal.}$$

At 1760° C. it was possible to saturate a 75-mil sample of molybdenum with nitrogen at 1 atm. pressure in 30 min. The time necessary for saturation with carbon monoxide appeared to be very much longer. For a 4-hr. heating period the amount of carbon monoxide absorbed was a linear function of time with no sign of saturation. At 1760° C. molybdenum absorbed in 30 min. eight times as much nitrogen as carbon monoxide and the nitrogen was desorbed in one-half the time taken by the carbon monoxide.

m
m

b
fc
p
tl

w
a

T

d

T

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Influence of Gases on Metals and Influence of Melting in Vacuo*

By Wilhelm Rohn,† Hanau, Germany

(New York Meeting, February, 1932)

In discussing the influence of a content of gases on metals and alloys we should probably first consider the physical and chemical conditions under which these gases may be present. By a chemical analysis, such as the total extraction of gases from the liquid metal by melting in a graphite crucible in vacuo, we find only the sum of gaseous chemical elements contained in the metal in any form and no reference is made to the special form under which they have been present previously.

Condition of Gases in Metals

In considering gases in metals we may first turn our attention to gases simply dissolved. Because the solubility of almost any gas decreases suddenly at the freezing point, most of them are released during solidification, developing rise of ingots and blowholes. If only a little gas is dissolved in the molten metal the size of such blowholes may be miscroscopical, or even submicroscopical, resulting in a certain reduction of the notched-bar impact test values. Hydrogen is believed to become less soluble as the temperature is lowered and therefore increasing quantities of this gas may be evolved during cooling between the freezing point and room temperature, leading to unsoundness of the ingot at weak spots; *i.e.*, at the grain boundaries. This gas at the grain boundaries probably is present at high pressure and therefore impairs the mechanical properties to a degree similar to that found in the hydrogen embrittlement of copper. Usually we may trace such gases by observing rising ingots, or at least by the formation of a characteristic pattern of small grooves upon etching.

Another condition of gases present within metals is that of chemical compounds, the most common being oxides and mostly present as slag inclusions of various kinds. If such oxides are insoluble in the liquid metal and emulsify with it, we find microscopical or submicroscopical slag inclusions distributed homogeneously throughout the metal and spread through the whole mass of the crystals. This special form does little harm to the mechanical properties. Some oxides are somewhat soluble in the liquid metal, but less in the solid state and these therefore accumulate during solidification in the grain boundaries, resulting in an intercrystalline brittleness. This may be regarded as the most unfavorable influence of gases in metals. By the addition of some manganese or silicon for the purpose of deoxidation we try to alter the nature of the oxides by transforming soluble oxides into insoluble ones that form the less harmful emulsion. If we could keep the liquid metal quiet for a sufficiently long time, these insoluble oxides would rise to the surface and adhere there to the slag layer covering the metal bath; unfortunately such quiescence is, in the usual melting practice, connected with an additional contamination of the metal through the formation of additional oxide.

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* Printed without author's corrections. Subject to revision.

† Director, Heraeus Vacuumschmelze, A. G.

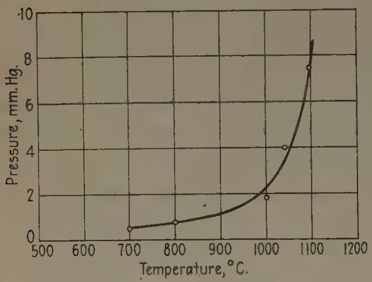


FIG. 1.—PRESSURE OF OXYGEN OVER COPPER OXIDE.

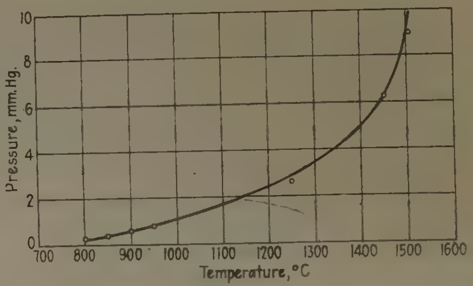


FIG. 2.—PRESSURE OF OXYGEN OVER NICKEL OXIDE.

In this connection, sulfur also may be regarded as a gas, because sulfur would be a vapor at melting temperature. This element gives one of the most typical illustrations of a partly soluble compound when present in molten nickel and later brought out as brittle layers between the crystal grains during solidification. An addition of manganese results in the formation of manganese sulfide, which shows a decreased solubility of the sulfide in the molten metal and therefore improves the workability. By adding a small amount of magnesium, a magnesium sulfide is formed, which is nearly completely insoluble in the molten nickel and thus forms the type of emulsion that influences the mechanical properties very slightly, if at all, resulting in the remarkable improvement in workability.

CAUSES OF GASES IN METALS

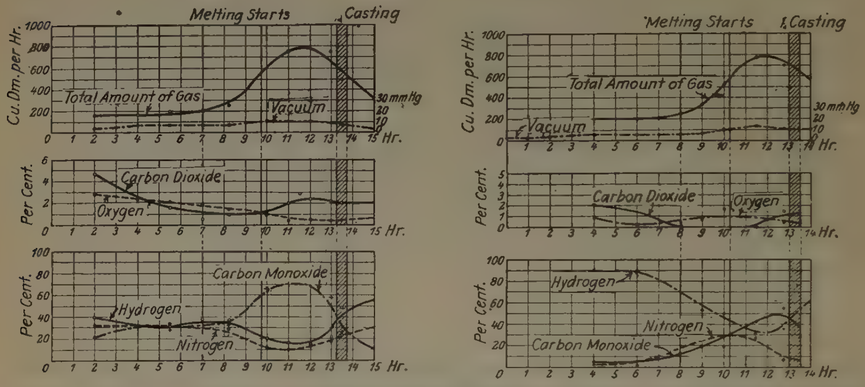
If the metal has been treated carefully during melting and before pouring, both these effects of gases may be easily avoided. The second kind is developed during the total oxygen analysis by the chemical reaction between the oxides and the graphite of the crucible or the carbon content of the pig iron we usually add to decrease the melting point of the mixture. We would scarcely find this kind of gas when simply melting the test piece in a crucible of alumina unless the vacuum is sufficient to decompose physically some of the oxides present in the molten metal. This spontaneous decomposition of oxides occurs, however, with cuprous oxide (CuO) even at 1100° C. and below 7 mm. mercury pressure; with nickel oxide it occurs at 1500° and 6 mm. mercury pressure, while even iron oxide is decomposed at 1600° C. and a pressure below 2 to 3 mm. The partial pressure of oxygen above the oxides of copper and nickel under equilibrium conditions at increasing temperatures is shown in Figs. 1 and 2. Probably even the oxides of manganese would decompose partly or totally at pressures below those usually applied on this special analysis, as for instance $1/100$ mm. at 1600° C. By stepwise decreasing the pressure during the analysis, it may become possible in the future to determine with which chemical element of an alloy the oxygen has been actually combined. Special care has to be given that no oxygen may be developed by chemical reaction between a crucible containing alumina or silicon dioxide and traces of carbon possibly present in the metal to be analyzed.

There is still another reason to be considered for the development of gases during analysis. We should not forget that no product of a commercial melting process has ever reached an actual equilibrium and even if this by chance should occur during melting at some special temperature, such equilibrium would be disturbed at once as soon as the metal cooled for solidification. Really, by far the major part of the gases we may find by analysis result from a continuation of chemical reactions which were uncompleted during the original melting process. We are very well aware that mild steel usually contains about 0.07 to 0.02 per cent C as well as 0.03 to 0.08 per cent O at the same time, although if complete equilibrium were attained, one of them should have practically disappeared, and only the excess of the other one should remain. The relative proportions of these two elements in commercial metals depends entirely upon the specific conditions of the preceding melting process.

It is very easy to understand that remelting under varied conditions—*e. g.*, melting under reduced pressure for gas analysis purposes—alters the equilibrium because of the removal of the gas phase and must therefore unavoidably lead to a remarkable development of gases, and here we have the real origin of most of the gases we find by the usual method of gas analysis. It is known, from previous experiments involving the magnetic properties of iron impaired as well by carbon as by oxygen, that annealing for a long time under reduced pressure enables carbon and oxygen to react together with a certain volatilization of both as carbon monoxide.

Figs. 3 and 4 show the amount and the composition of gases driven out by melting in a vacuum furnace from charges weighing 3500 kg. each.

The maximum evolution of gas does not occur as soon as the whole charge becomes liquid, but instead, the rate increases for another 2 hr., showing that these gases result from chemical reactions, which become more complete under vacuum conditions. By far the greatest part of the gas is carbon monoxide, which probably comes from a reaction between traces of carbon and of oxides contained in the raw materials. The hydrogen, on the other hand, may at least partly result from traces of water vapor and moisture decomposed by the hot metal.



FIGS. 3 AND 4.—AMOUNT AND COMPOSITION OF GASES DRIVEN OUT BY MELTING IN A VACUUM FURNACE.

Fig. 3.—Charge: 3500 kg., of which 1500 kg. was first melted in vacuo. New material was 2000 kg. Ni and Cr. Total amount of gas = 5200 cu. dm. = 2.6 cu. dm. per kg.

FIG. 4.—Charge: 3500 kg., of which 500 kg. was first melted in vacuo. New material was 2500 kg. Ni and 500 kg. Cr. Total amount of gas = 4000 cu. dm. = about 1.35 cu. dm. per kg.

MELTING IN VACUO

To regard somewhat more in detail the effect of commercially melting steel and other metals and alloys in vacuo, we have to consider three kinds of gases separately. The first group is typified by hydrogen dissolved in palladium, hydrogen contained in electrolytic iron (somewhat similar to that found in iron after pickling) or perhaps exemplified by oxygen dissolved in molten silver or sulfur dioxide in molten copper. A part of these gases simply comes out during melting in vacuo, principally just as the solid metal changes to the liquid; another part is given off during solidification. For this reason such metals should be melted in vacuo, allowed to solidify again and afterwards remelted and cast in vacuo to avoid any contamination by further influence of air of furnace gases.

The second kind of gases is much more difficult to bring out; as mentioned above, some oxides are decomposed by the simple influence of a vacuum treatment under a sufficiently reduced pressure. In this way plain copper, nickel or iron may be easily purified. For example, vacuum-melted copper does not contain any oxygen and for this reason it is never sensitive to hydrogen embrittlement.

But it seems to be very improbable that we shall be able in the near future to carry out vacuum melting on a commercial scale at such a reduced pressure as to decompose even the oxides of chromium, silicon or aluminum. Chromium oxide (Cr_2O_3) seems to be insoluble in molten steel and does not so much harm the mechanical qualities of the finished metal, so that chromium might be used as a deoxidizer to a greater extent, provided that no silicon is present. To remove such oxides, the only way at present seems to be the application of strong reducing elements such as hydrogen or carbon, the excess of which is to be removed afterwards.

For such metals, melting in vacuo offers a further advantage in enabling us to keep the metal quiet for a long time (allowing the particles of oxides and slag to rise to the surface) without contamination by air. Just this possibility of keeping a molten metal quiet for a period as long as may be desired without any contamination may be regarded as an important advantage of vacuum melting.

Such an improvement is not achieved by simply putting a ladle containing liquid metal under an evacuated bell, as sometimes suggested in the past, because the metal cools too quickly to permit an effective vacuum treatment for a sufficiently long time. Therefore for this purpose it is necessary to employ actual vacuum melting, in a vacuum furnace, which allows the metal to be heated up in vacuo and to be kept hot for a sufficiently long time.

In the case of the third type of gas content, we can expect the most direct and visible influence of a vacuum treatment, because the chemical reactions, the products of which are gaseous, become more complete and the real equilibrium is much more nearly reached. In a steel containing carbon and oxygen or oxides at the same time we may be sure that one of them will disappear nearly completely. Any excess of oxygen can be taken off afterwards by reducing the pressure below 2 mm., providing that no oxides of silicon or aluminium are present. A remaining excess of carbon can be taken off only by addition of oxygen, any excess of which *must* be removed afterwards as described above.

ADVANTAGES OF VACUUM MELTING CONFIRMED BY IMPACT TEST

The improvement of metals and alloys by melting in vacuo can be confirmed by the increased values of a notched-bar impact test. Test pieces taken from various different points of the cross-section of an ingot produced by carrying out melting and casting in vacuo show more uniform values and a higher average than those taken from an ingot of the same size cast from the same melt but without vacuum treatment. In some cases the values of notched-bar impact test of pieces taken from the ingots themselves showed an increase of 40 to 100 per cent, while even after rolling for a total reduction of more than 20 or 30 times the increase was still 20 to 35 per cent, compared to values obtained from the same melt but without treatment under vacuum. A similar improvement is shown by a fatigue test. Some actual values may be given which were obtained on a nickel-chromium alloy containing 15 per cent Cr, 20 per cent Fe, 2 per cent Mn, 63 per cent Ni. Such an alloy was melted with special care in an arc furnace and cast to an ingot of 300 kg. From different points of the cross-section notched-bar impact test pieces 60 by 10 by 10 mm. (corresponding to the small Charpy test piece) were taken, and an average of 3.4 m-kg. per sq. cm. was found. The rest of this ingot was then rolled from 200 mm. dia. to 15 mm. and from this rolled rod another series of tests was made averaging 11.8 m-kg. per sq. cm. The same alloy was melted in vacuo from exactly the same raw materials and cast to ingots of exactly the same size. If the rate of solidification was slow, by casting in a ceramic mold test pieces from various points of the cross-section gave an average of 11.4 m-kg. per sq. cm. and if casting was carried out in a water-cooled copper mold the results averaged to 13.9 m-kg per sq. cm. Parts of these ingots rolled from 200 to 15 mm dia. showed values of 22 and 26 m-kg per sq. cm. respectively. The vacuum-melted material is proved therefore to be far superior in every condition; as cast as well as in the rolled condition.

Practical Application of Vacuum Melting

To raise, finally, the question as to whether it might be possible to introduce vacuum melting into actual practice in the not too far distant future, it must be said that it seems to be impossible because of cost, if we start with cold charges. Even with furnaces for 4 tons, two of them having been now in constant use for about nine years, the increase in melting costs amounts to about ten cents per pound of ingots, which doubtlessly is a prohibitive figure for ordinary melting practice. But the technique has been developed so far that it would be possible to start such furnaces with molten metal from other sources, carrying out only the last refinement and the casting in the vacuum furnace. Under such conditions the increase of costs may be expected to be reduced to between one and two cents per pound, and such a figure may perhaps pay for some special purposes, where an increased quality is more essential than a somewhat higher price. The present technique of vacuum melting has been developed far enough to be introduced now for such special purposes, and perhaps we may expect that soon steels and alloys for special and highly important parts (such as blading for turbines, tubing for superheaters for highest pressures and temperatures and parts of airplanes) may be produced by vacuum melting.

Influence of Gases on Metals and Influence of Melting in Vacuo*

By Wilhelm J. P. Rohn,† Hanau, Germany

(New York Meeting, February, 1932)

Abstract

When a metal solidifies, gas, initially present in solution, may be concentrated at the grain boundaries, leading to brittleness, or it may form solid compounds which, if localized at the grain boundaries, impair the properties. On the other hand, the solid compounds formed sometimes distribute themselves more or less uniformly, and hence may be relatively harmless.

If metallic oxides are heated under a partial oxygen pressure less than that corresponding to the dissociation pressure of the oxide in solution in the melt, they will decompose and oxygen will tend to be eliminated from the melt. This paper presents data on the partial oxygen pressures of copper and nickel oxides over a wide range of temperatures; it also presents data regarding the amount and nature of the gases evolved in the vacuum melting of a 3500-kg. charge of nickel-chromium alloy and gives test values indicating the improvement in impact values ascribed to vacuum melting.

The results of commercial experience with a 4-ton vacuum melting and casting furnace indicate that this method entails an increase in cost of about 10 cents per pound of ingot over orthodox practice, which may be justified for special products and may be lowered if hot metal is charged into the vacuum furnace.

DISCUSSION

(Howard Scott presiding)

J. H. Scaff, New York, N. Y. (written discussion).—In the section of Dr. Rohn's paper describing the effect of melting metals in vacuo, he says, "In this way plain copper, nickel and iron may be easily purified. For example, vacuum-melted copper does not contain any oxygen and for this reason it is never sensitive to hydrogen embrittlement." This statement is contrary to the results of our experiments at the Bell Telephone Laboratories on the effect of vacuum melting on the properties of copper. Several 150-gram samples of tough-pitch copper were melted in a vacuum of the order of 1×10^{-5} to 1×10^{-6} mm. Hg for 2 hr. Portions of the ingots obtained were swaged to 0.100 in., then drawn to wire 0.050 in. in diameter for physical and electrical tests. The specimens were not annealed during working. When wires made in this way were annealed at 850° C. for ½ hr. in hydrogen they were embrittled, showing that the oxygen had not been removed by the vacuum treatment.

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* This paper is available at the office of the Institute as *Technical Publication No.* 470.

† Director, Heraeus Vacuumschmelze, A. G.

These results can be explained as follows: Even though the pressure of oxygen above pure cuprous oxide may be of the order of 1 mm. Hg at the melting point of copper, the oxide is soluble in molten copper and the pressure of oxygen above the dissolved cuprous oxide is much lower than that over pure material. We believe the pressure of oxygen above copper containing 0.04 per cent oxygen must be below 1×10^{-5} mm. Hg.

R. C. Dalzell, Trenton, N. J.—I presume that the vapor-pressure curve given in Fig. 1 is that of CuO, not Cu_2O. If the former, it has no bearing on oxide in molten copper, as it is well established that CuO is completely converted to Cu_2O below 1087° C. If the curve is actually supposed to be that of Cu_2O, I fear that Dr. Rohn has chosen an unreliable authority (which he does not give). The references on this point are covered in A.I.M.E. *Tech. Pub.* 478, by O. W. Ellis. I am inclined to suspect that the curve for nickel oxide may be as erroneous, but have not looked into this.

Dr. Rohn states further, on page 7, that vacuum-melted copper does not contain any oxygen, and for this reason is not subject to hydrogen embrittlement. He has been misinformed on this subject as well. I have seen copper that has been melted and cast in vacuum which most certainly did contain oxide, and was just as susceptible to hydrogen embrittlement as ordinary copper.

W. J. P. Rohn (written discussion).—It is difficult for the author to give any definite suggestion with regard to the discrepancy between the results about hydrogen embrittlement of vacuum-melted copper that were obtained by Mr. Scaff and Mr. Dalzell and those obtained by himself, inasmuch as such results may be widely influenced by small incidental impurities. Actually the author found a copper carefully melted in vacuo as not being subject to hydrogen embrittlement, and such copper was for some time in commercial use for purposes where hydrogen embrittlement had to be avoided.

The author is especially glad to learn from other A.I.M.E. papers that important investigators agree that in metals the actual solubility of gases as such is at least very small and that most of the gases developed under fusion in vacuo result from chemical reactions.

Preprint.—American Institute of
Mining and Metallurgical Engineers.

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Some Metallurgical Characteristics of Induction Furnaces as Determined by the Absorption of Oxygen by Molten Nickel

By F. R. Hensel,* Pittsburgh, Pa. and J. A. Scott,† Harrison, N. J.

(New York Meeting, February, 1932)

The absorption of oxygen by molten metals is a quick and convincing method to determine the metallurgical characteristics of various types of furnaces.[1] The investigation was restricted to the use of coreless induction furnaces. A major variable in induction furnace practice is the frequency and its influence was studied by comparing melts made in a 5000-cycle and a 60-cycle induction furnace respectively.[2] The authors are not aware that such a comparative study has been made before and therefore present this paper in the belief that the results will be of general interest.

Analytical Methods for Determination of Oxygen in Nickel

An analytical procedure for determining NiO by a quick and simple laboratory method has been worked out in collaboration with Dr. Herty of the Pittsburgh Station of the Bureau of Mines. It was found that Dr. Herty's aluminum method as used for the determination of FeO in iron and steel was very suitable for use with nickel if instead of hydrochloric acid a 10 per cent solution of nitric acid is used for bringing the metal into solution. Essentially this method involves deoxidizing the nickel-oxygen alloy with aluminum ($2Al + 3NiO = Al_2O_3 + 3Ni$) and determining the resulting Al_2O_3 by a residue analysis. The original oxygen content can then be calculated from the amount of Al_2O_3. The method as suggested by Dr. Herty[3] is referred to in the present paper as method B. A slight modification of method B led to the application of method A, a description of which is given below according to F. W. Beiter‡:[3]

The sample, the size of which is regulated by the amount of Al_2O_3 present, is treated with 55 c.c. of 10 per cent HNO_3 for each 2 grams taken, and heated to about

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* Group Engineer, General Metallurgical Group, Westinghouse Research Laboratories.

† Driver-Harris Co.

‡ Analyst in the Chemical Division, Westinghouse Research Laboratories.

[1] C. H. Herty, Jr.: Carnegie Inst. of Tech. *Bull.* 34, 36, 37, 38, 44, 46, 51.

[2] Nickel was chosen as test material for the experimental melts because the 60-cycle furnace was used commercially for the production of nickel and nickel alloys.

[3] A detailed description of the method is given in *Trans.* A. I. M. E., Iron and Steel Div. (1930) 28–44.

70° C. overnight. In the morning 1 c.c. of strong HNO_3 is added for each 2 grams of sample and the heating continued till the next morning. At this time the sample should all be in solution and the acidity of the liquid will be about 2 per cent.

After filtering through a close paper, with paper pulp added, washing well with cold H_2O, igniting and weighing (per cent residue), the residue is fused, with 15 times its weight of Na_2CO_3, for ½ hr. The soluble part of the fusion is now extracted with 100 c.c. H_2O and the solution filtered. The residue is ignited and again fused with Na_2CO_3 for ½ hr. After leaching and filtering into beaker containing the original filtrate, the residue is ignited, and if it is light in color or weighs more than 5 mg. it is fused with $KHSO_4$ and the solution tested for Al_2O_3 by the phosphate method.

The Na_2CO_3 solution from the two fusions is made acid with HCl, evaporated to dryness to dehydrate the silica and taken up with 25 c.c. 1:1 HCl and 50 c.c. H_2O. The silica is then filtered off and the Al_2O_3 precipitated with NH_4OH in slight excess After filtering the precipitate is dissolved in 100 c.c. of 5 per cent HCl and a second precipitation carried out with NH_4OH. After filtering and washing well with 3 per cent NH_4NO_3 ignite and weigh as Al_2O_3.

The analytical problem was attacked in another way by W. C. Weltman, Analyst in the Chemical Division, Westinghouse Research Laboratories, with the object of finding an electrolytic method for determining Al_2O_3. His report of the results is as follows:

The method is based on the U. S. Bureau of Mines' procedure for the determination of nonmetallic inclusions in iron and steel. For iron and steel the electrolyte consists of an aqueous solution of ferrous sulfate plus sodium chloride. Therefore, in attacking this problem the first electrolyte used consisted of an aqueous solution of nickelous sulfate plus sodium chloride. This proved unsatisfactory because the pH of the nickel sulfate electrolyte rises rapidly from its original value of about 4 to 7.5, resulting in the precipitation of a heavy sludge of nickelous hydroxide plus basic nickel sulfate. The nickel content of the electrolyte decreased in 16 hr. from 30.0 g. per liter to 16.9 g. per liter, estimated as $NiSO_4 \cdot 7H_2O$. No nickel deposited on the cathode; hydrogen was freely evolved during the electrolysis.

The nickel samples—the anodes—had been deoxidized with metallic aluminum in excess and so contained a considerable proportion of metallic aluminum in addition to the Al_2O_3. This aluminum, going into solution as Al^{+++}, precipitated as $Al(OH)_3$ when the pH rose above about 5.5. Some of this precipitation took place within the collodion bags, giving high and erratic values for Al_2O_3.

Various reagents were added for the purpose of keeping the pH of the electrolyte below 5.5. Boric acid to the amount of 1 per cent had practically no effect on the pH, and did not keep the pH from rising to 7. Sufficient sulfuric acid was added to bring the pH down to 2.0 but in 16 hr.—the time of a run—the pH again rose to 7, nickel and aluminum hydroxide being precipitated. A current of 0.8 amp. was used.

Tartaric acid lowered the pH satisfactorily, and while the pH rose during a run it rose slowly and no hydroxide precipitated.

It was found that when ammonium chloride was substituted for sodium chloride, the nickel deposited on the cathode in an adherent coat.

The composition of the electrolyte as finally worked out was: $NiSO_4.7H_2O$, 40 to 50 g. per liter; tartaric acid, 10 g. per liter and NH_4Cl, 10 g. per liter.

Of secondary importance to this investigation was the observation that the concentration of the solution in nickel could be controlled by the amount of free tartaric acid present, as shown by the data.

COMPOSITION OF ELECTROLYTE

	$NiSO_4.7H_2O$, Grams per Liter		Tartaric Acid, Grams per Liter
	pH		
At start	1.7	44.3	10
After 1st run	5.30	59.6	2.5 added after 1st run
After 2nd run	4.88	56.8	None added after 2nd run
After 3rd run	5.58	51.0	None added after 3rd run
After 4th run	6.18	31.0	2.5 added after 4th run
After 5th run	5.58	44.0	

At about pH 5.5, nickel begins to plate out faster than it dissolves at the anode. By making occasional pH determinations, and adding tartaric acid as indicated, the nickel content of the bath can be maintained constant and the bath used until too much tartaric acid accumulates. No data have been obtained as to the saturation point of tartaric acid.

The results of the "aluminum method" agree very closely with those of the vacuum fusion method[4] as evident from Fig. 1. In Fig. 2, a comparison of the analytical results obtained with methods A and B is given, while in Fig. 3 the analytical results according to method A and the electrolytic method are plotted.

The agreement among the four methods is fairly close. Besides the vacuum fusion method, the method A is the most accurate one, while the results of method B as well as of the electrolytic method are somewhat on the high side.

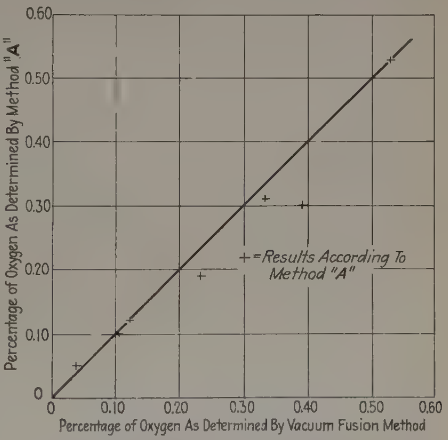

FIG. 1.—COMPARISON OF VACUUM FUSION METHOD WITH ALUMINUM METHOD.

The difficulties of Al_2O_3 segregation within the test piece were overcome by milling the entire length of the test ingots on one side so that the chips represented top, middle and bottom of the ingot as well as outside and inside.

SOLUBILITY OF OXYGEN IN MOLTEN NICKEL

For determining the solubility of oxygen in molten nickel, 10 lb. of electrolytic nickel was melted down in a small Ajax high-frequency furnace. Nickel oxide was then added in sufficient quantity to form a slag of pure NiO on top of the melt. At a chosen temperature, measured by means of a platinum, platinum-rhodium thermocouple, the slag was quickly removed and the metal poured into a preheated ladle and deoxidized. The ladle held about 2 kg. of metal. Pure aluminum wire of ¼-in. dia. was used for deoxidation. Sufficient wire was added to secure complete deoxidation and leave some excess of aluminum to be taken into solution by the nickel.

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[4] Data obtained by N. A. Ziegler.

Because of this deoxidation with aluminum the metal became viscous and was difficult to pour. At temperatures near the melting point the viscosity became so great as to make pouring nearly impossible. Under these conditions trapping of slag particles within the solidifying metal could not be wholly avoided and the oxygen results are therefore high for the temperatures near the melting point, as shown in Table 1. Although the points are somewhat scattered, there is a definite trend of increasing solubility of nickel oxide with the temperature.

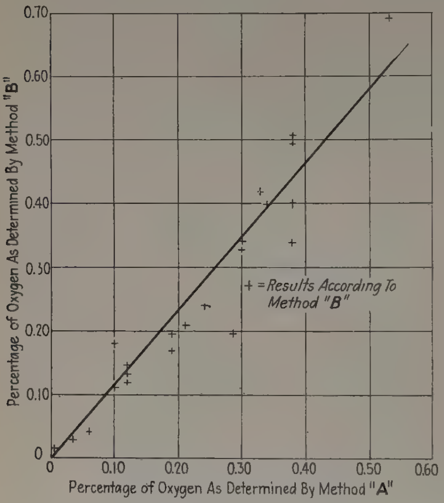

FIG. 2.—COMPARISON OF METHOD A WITH METHOD B.

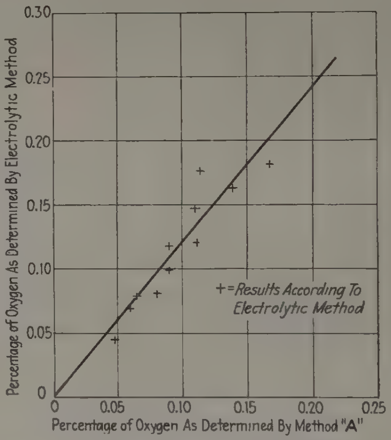

FIG. 3.—COMPARISON OF METHOD A WITH ELECTROLYTIC METHOD.

TABLE 1.—*Solubility of Oxygen in Molten Nickel at Various Temperatures*

Mark	Temperature, Deg. C.	Oxygen, Per Cent	
		Method A	Method B
2	1465	0.33	0.42
3	1510	0.38	0.35
4	1550	0.34	0.40
28	1550	0.38	0.51
5	1590	0.38	0.41
6	1650	0.53	0.69

More accurate results were secured by means of the vacuum fusion method. Some of the data so obtained were as follows:

Temperature, Deg. C.	Oxygen, Per Cent
1465	0.294
1550	0.423
1650	0.526

Fig. 4 shows that there exists a nearly linear relationship between the solubility of oxygen in nickel and the temperature. It is very striking that nickel behaves in this respect almost as does iron. It must be borne in mind, however, that the melting point of iron is about 80° C. higher than that of nickel. A given temperature, therefore, means quite a different amount of overheating for Ni-NiO than for Fe-FeO, and it should be expected that at the same temperature the solubility of NiO in nickel will be higher than that of FeO in iron if the solubility coefficients are about the same.

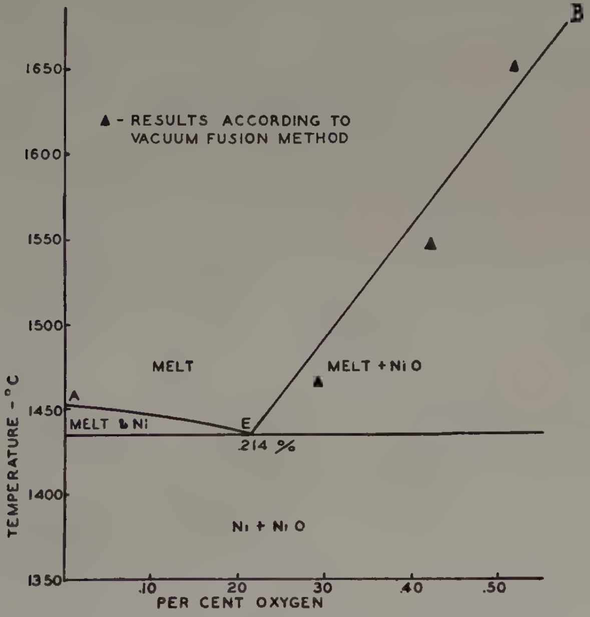

Fig. 4.—Tentative nickel-oxygen diagram.

The melting points of nickel-oxygen alloys are lower than for pure nickel because of the formation of a eutectic between NiO and Ni which according to our measurements lies at 1435° C., while the melting point of pure nickel is 1452° C. According to the literature,[5] the eutectic oxygen concentration was found to be 0.214 per cent.

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[5] Merica and Waltenberg: *Trans.* A. I. M. E. (1925) **62, 709.**
Masing and Koch: *Ztsch. f. Metallkunde* (1927) 278.

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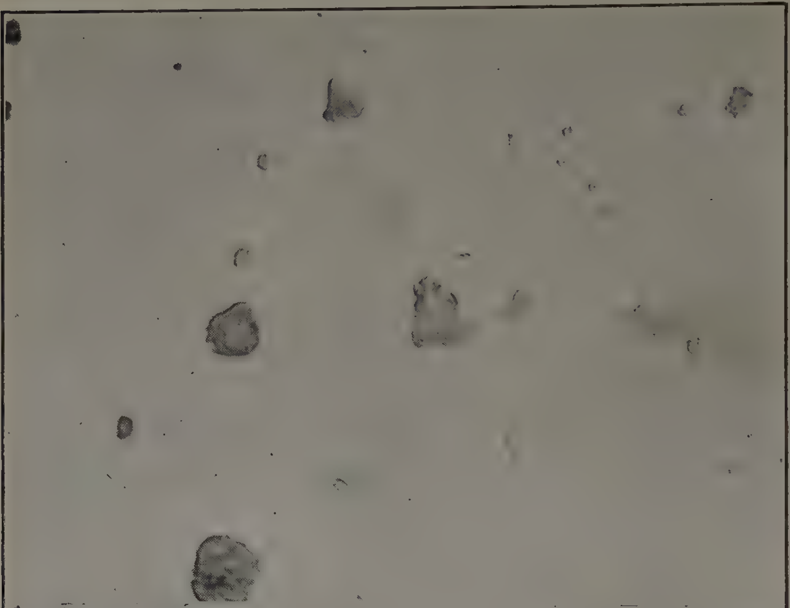

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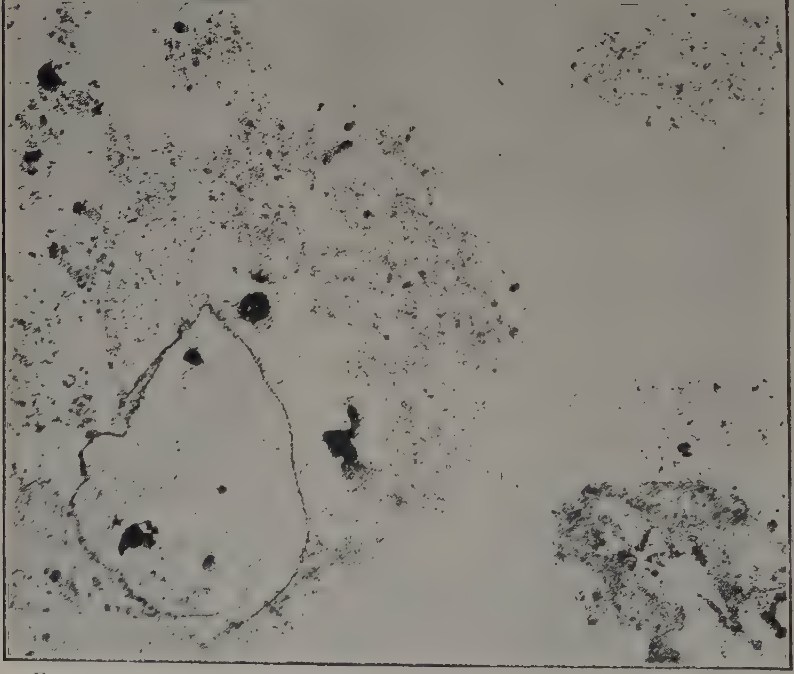

FIG. 5.—SAMPLE SATURATED WITH NICKEL OXIDE (HEAT 156). × 1000.
FIG. 6.—SAMPLE DEOXIDIZED WITH ALUMINUM. × 100.

The microscopical investigation of some of the alloys containing over 0.21 per cent oxygen in the nondeoxidized state revealed the presence of large plates of nickel oxide separating along the line *EB* while a fine eutectic formed at the point *E* of Fig. 4, as indicated in Fig. 5. After deoxidizing with aluminum no typical nickel oxide could be detected, as all of it had been converted into Al_2O_3 arranged in the typical form of clusters shown in Figs. 6 and 7. The nickel oxide plates and the eutectic separated generally within the grains and not along the grain boundaries.

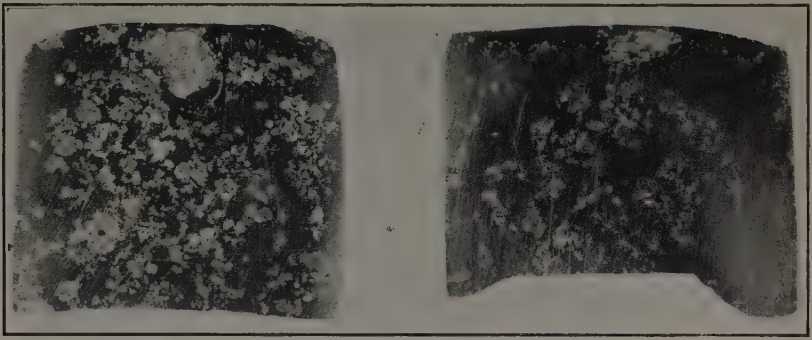

FIG. 7.—POLISHED TEST SAMPLES DEOXIDIZED WITH ALUMINUM. Al_2O_3 ARRANGED IN TYPICAL FORM OF CLUSTERS.

EFFECT OF AGITATION ON OXYGEN PICK-UP DURING MELTING

A 60-cycle tilting furnace holding a charge of approximately 700 lb. of metal and a 5000-cycle tilting furnace with a capacity of 250 lb. were used for determining the relative rates of oxygen pick-up with different degrees of turbulence. The pouring spout and a hole in the lid of both furnaces were left open, allowing a continuous draft which insured a sufficient supply of air in contact with the liquid metal surface. The crucibles used in the 60-cycle furnace were made of magnesium oxide and had an average inside diameter of 15¾ in. For the 5000-cycle furnace, zirconium silicate crucibles with an average inside diameter of 9⅝ in. were employed. Although the crucible dimensions and the weights of the charges are different in the 5000-cycle and 60-cycle furnaces, it is possible to obtain a comparison between the two on the basis of the respective surface areas exposed to air per unit weight of charge. This area was found to be approximately the same for both furnaces, assuming a 700-lb. charge in the 60-cycle furnace and a 250-lb. charge in the 5000-cycle furnace. It amounts to 4.11 sq. cm. per kg. for the 5000-cycle furnace and 3.96 sq. cm. per kg. for the 60-cycle furnace.

Samples were taken from the molten baths by means of special wrought-iron tubes. These were 1¼-in. inside diameter, closed on one end, sand-blasted on the inside and outside and painted with a high-temperature cement (consisting mainly of SiO_2) on the closed end. About

5 in. from the closed end two large holes were drilled in the tubes to allow liquid metal to fill the interior upon immersion in the melted nickel. These sampling tubes were preheated to 500° to 600° C. and then dipped into the metal bath far enough to allow liquid metal to fill the lower parts of them. While the tubes were being removed from the molten bath 10 to 12 in. of ¼-in. dia. pure aluminum wire was inserted into the still liquid metal within them, thus effecting complete deoxidation. In order to secure a fast cooling rate and so avoid pick-up of extraneous oxygen, the tubes were plunged into water after deoxidizing. A number of check tests were made which showed that this method secured test samples showing the same Al_2O_3 content as did samples deoxidized in a small preheated ladle.

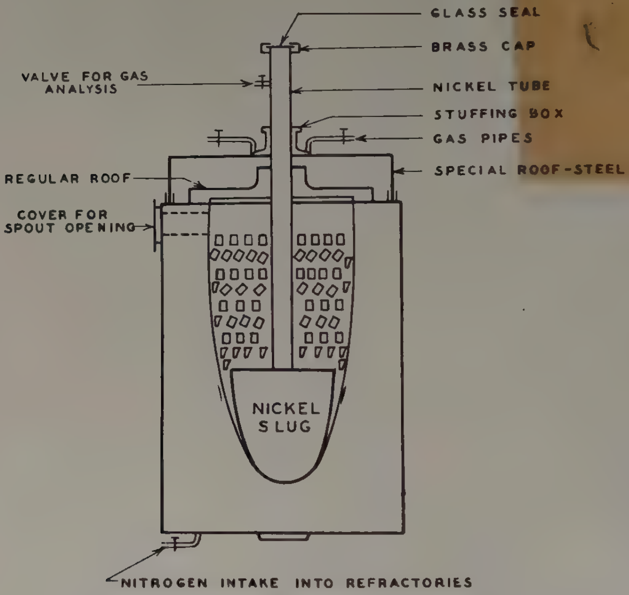

FIG. 8.—ARRANGEMENT OF CLOSED 60-CYCLE FURNACE.

In order to get test samples from the bottom pool, generally formed first in the 60-cycle furnace, a nickel tube was inserted into the charge in the manner shown by Fig. 8. Charging was done in the following way: A nickel slug weighing about 300 lb. was first placed in the furnace. In the center and resting on top of it a nickel pipe 2½-in. outside diameter was placed. This was long enough to extend 1 ft. above the furnace roof through a special stuffingbox which enabled a tight seal at the lid for the experiments that were made under a controlled atmosphere. After the nickel tube had been set in place, the rest of the nickel in the form of small plates of electrolytic nickel was charged around it. A new nickel tubing was required for each experiment, as in each one the lower part of it melted down with the charge.

The temperatures were measured with a platinum, platinum-rhodium thermocouple, which in the 60-cycle furnace was inserted far enough to touch the nickel slug and in the 5000-cycle furnace was placed on top of the charge, which consisted entirely of electrolytic nickel. In the 60-cycle furnace the top of the charge showed a temperature of not more than 40° C. when the nickel slug on the bottom was just melting.

For checking the thermocouple readings, comparative measurements were made with the Pyrovisor, a new instrument manufactured by Stroehlein & Co., Dusseldorf, Germany. The fairly close agreement of the data obtained can be seen from Table 2.

TABLE 2.—*Comparison of Results with a Platinum, Platinum-rhodium Thermocouple and a Pyrovisor*

THERMOCOUPLE	PYROVISOR
1540° C.	1538° C.
1550° C.	1516° C. (slag)
1595° C.	1538° C. (slag)
1670° C.	1650° C.
1690° C.	1700° C.

Results Obtained with the 60-*cycle Furnace Operated in Air Atmosphere*

Two experiments were run, the results of which checked each other closely. The data of experiment 2 are plotted in Fig. 9.

The interpretation of the curves is largely self-evident. Of main interest is the oxygen pick-up during the melting period. Immediately after a liquid bottom pool is formed we find a very low oxygen content. The rate of increase in oxygen content is small until the entire charge has melted, because the molten Ni-NiO mixture is being diluted continuously by the melting down of the electrolytic nickel with its very low oxygen content. Moreover, it so happened that the nickel charge contained about 0.10 per cent Si, which protected the nickel from oxidizing in the first melting stages. After a certain time, approximately 30 to 40 min. after melting started, the oxygen pick-up became proportional to the time. This portion of the oxygen-time curve is nearly a straight line, reaching the saturation limit of nickel for nickel oxide in 40 to 50 min. after melting is complete when minimum stirring action in the bath is provided by operating at a reduced voltage, which gave a power input of 50 kw. The time required to reach saturation would probably be considerably shorter with the more vigorous stirring action that accompanies higher power input.

Of the two sets of oxygen-concentration data, that obtained by method A seems to be more in agreement with the probable facts, as it can be assumed that the oxygen pick-up curve will flatten out when it reaches the saturation limits. The shape of the power curve *KW* is a sufficient indication of the furnace conditions up to the melting point. As soon as this curve reaches a minimum and starts to rise there is a definite indication for the beginning of melting. In the initial charges of the diameter used in the heats reported, an increase in temperature is accompanied by a decrease in power input to the charge except in the low-temperature range up to 350° C. where the metal is magnetic. The power input also varies almost as the square of the diameter of the charge for a given furnace voltage, so that when melting commences and allows the charge to fill the entire cross-section of the crucible, the power input rises abruptly.

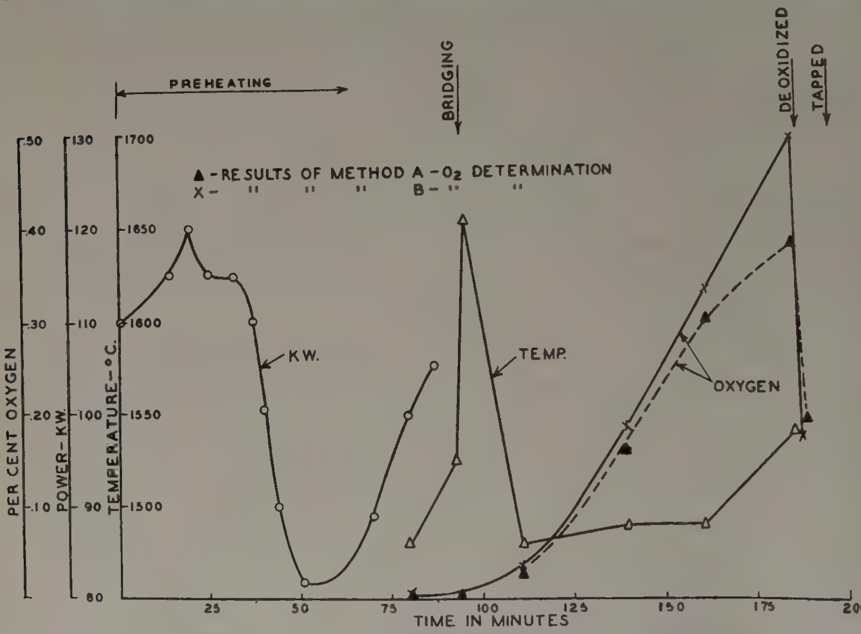

FIG. 9.—TEMPERATURE-TIME AND OXYGEN-TIME RELATIONS IN THE OPEN 60-CYCLE FURNACE.

It should be noticed that in Fig. 9 in an interval of 5 to 10 min. the temperature of the metal bath rose about 160° C. on account of bridging, which prevented the unmelted metal from settling down into the bath.

Fig. 9 is representative of an average production melt in an open furnace. The metal becomes nearly saturated with oxygen before tapping and an excessive amount of deoxidizer is required to reduce the nickel oxide formed.

Results Obtained with the 5000-*cycle Furance Operated in Air Atmosphere*

Two test runs were made, the results of which checked very closely. The data of run 1 are plotted in Fig. 10, which represents a melt comparable with the melts made in the 60-cycle furnace. After melting down the charge the temperature was held constant for about one hour. The temperature was 1550° C. instead of 1480° C., as in the previous cases. The power input was regulated by the current, since no kilowattmeter was attached to the melting unit. The nickel was charged gradually, as seen from Fig. 10, this being the reason for the relatively high oxygen content of the first test sample taken after melting down of the entire charge. The oxygen pick-up after melting down is a function of the time. The oxygen absorption curve differs greatly from that obtained with the 60-cycle furnace. It shows a much lower time rate of oxygen pick-up and the final value of the oxygen content is considerably lower than that obtained in the 60-cycle furnace. It stays well below the saturation limit of nickel oxide in nickel. By adding what is considered a normal amount of deoxidizer a very satisfactory degree of deoxidation was obtained.

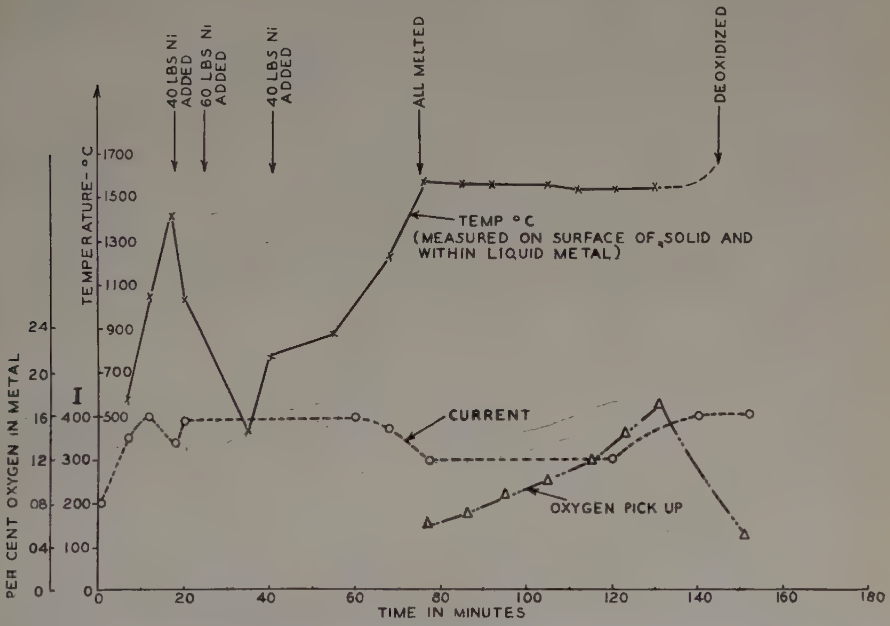

FIG. 10.—EXPERIMENTAL MELT OF ELECTROLYTIC NICKEL IN OPEN 250-LB. 5000-CYCLE INDUCTION FURNACE.

Discussion of Results

The difference in the absorption of oxygen in the 60-cycle and 5000-cycle furnaces is caused by the difference in the turbulence. For a given furnace and charge the turbulence is proportional to the power input and varies with the frequency approximately as represented by the equation

$$T = \frac{W}{\sqrt{f}}$$

where T is turbulence, W is power and f is frequency. The turbulence in a 60-cycle furnace is then about 10 times as great as in a 5000-cycle furnace of the same design, size and power input.

It is noteworthy that the mean oxygen pick-up of the 60-cycle furnace was but slightly more than three times as great as in the 5000-cycle furnace. If we call the oxygen absorption O, the turbulence T, the time t, the rate of absorption φ, we might write for the oxygen pick-up in an open induction furnace

$$O \propto T^x \times t^y \times \varphi \times K$$

where K is a constant.

From a physicochemical point of view, the problem is difficult to attack, as neither the law of mass action nor diffusion laws can be applied, for the reason that the law of mass action deals only with reversible reactions and the diffusion laws do not take into consideration mechanical agitation.

Although our empirical formula is not exact, it points to the importance of the following facts which have been proved experimentally beyond doubt:

1. The oxygen absorption is dependent upon the agitation or the rate of replacement of the exposed surface when air has free access to the surface of the melt.
2. Up to the saturation limit the quantity of oxygen absorbed is dependent upon the time of exposure of the molten metal to air.
3. The oxygen absorption is a function of the bath temperature and proceeds more rapidly the higher the temperature. The design of the furnace and the extent to which it is filled also have a great effect upon turbulence quite independently of frequency. However, the problem of selecting the optimum frequency is beyond the scope of this paper.

In the following section data are presented which indicate that the furnace atmosphere is of far more importance than frequency if really close control of oxygen pick-up is desired.

Effect of Furnace Atmosphere on Oxygen Pick-up

The set-up of the 60-cycle and the 5000-cycle furnaces for experimental heats melted under a protective nitrogen atmosphere can be seen from Figs. 8 and 11. The 5000-cycle unit in this case was a stationary furnace holding about 170 lb. of metal. The best results obtained in

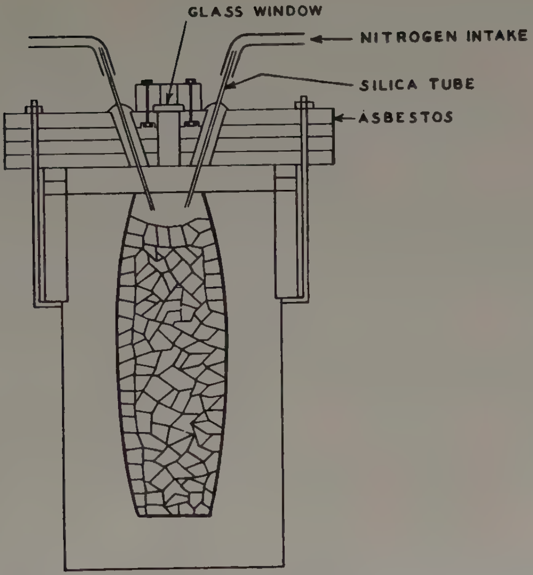

FIG. 11.—ARRANGEMENT OF CLOSED 5000-CYCLE FURNACE.

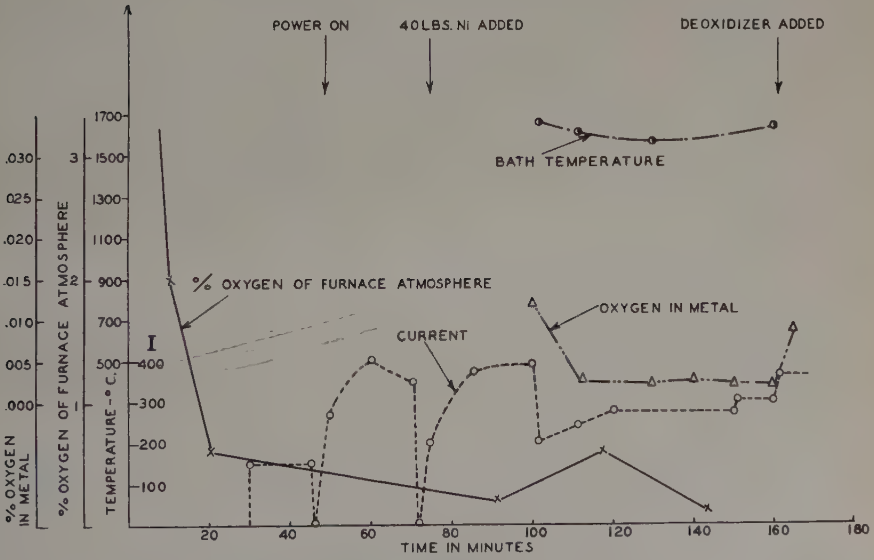

FIG. 12.—170-LB. NICKEL MELT UNDER NITROGEN ATMOSPHERE IN 5000-CYCLE INDUCTION FURNACE.

both types of furnaces were so much alike that only the data of the 5000-cycle induction furnace have been plotted in Fig. 12.

It was possible in both furnaces to control the oxygen content of the furnace atmosphere closely and to prevent pick-up of fresh oxygen.

The technical difficulties of setting up the furnaces for a run under a protective atmosphere were smaller than expected. It can be done easily under laboratory conditions. The feasibility of this procedure for production work is a question which will not be discussed here.

The influence upon oxygen pick-up by the nickel charge during melting under an atmosphere nearly oxygen-free is pronounced in both furnaces. No pick-up of oxygen was noticeable during a test period of more than 60 min., although the bath temperature was fairly high. The final oxygen content was below 0.003 per cent.

Melting under gaseous atmospheres includes the danger of contaminating the metal if the affinity or solubility of the metal for the protecting gas is great.

The results obtained showed that no nitrogen had been absorbed by the nickel bath. According to data obtained by the vacuum fusion method the samples contained from 0 per cent N_2 to 0.004 per cent N_2.

In this connection the interesting observation may be mentioned that in the open furnace the nitrogen absorption was a function mainly of the bath temperature, as judged by the following results obtained by means of the vacuum fusion method by N. A. Ziegler.

Sample No.	Temperature, Deg. C.	Nitrogen, Per Cent
2	1405	0.004
28	1550	0.023
6	1650	0.051

CONCLUSIONS

1. Herty's aluminum method slightly modified was found to be a very suitable means for determining the nickel oxide content in nickel.

2. An electrolytic method of determining Al_2O_3 in nickel was worked out.

3. The solubility temperature relations for nickel oxide in molten nickel were determined approximately. It was found that the solubility of nickel oxide increased with the temperature.

4. Comparative tests on the rate of oxygen absorption as effected by turbulence were made in a 60-cycle and a 5000-cycle furnace. The absorption of nickel oxide in nickel was found to be an increasing function of turbulence, time and temperature.

5. The rate of oxygen pick-up in the 60-cycle furnace is approximately three times as great as in the 5000-cycle furnace.

6. In the 60-cycle furnace the maximum oxygen content of the melt comes close to the saturation limit.

7. Melting under an oxygen-free atmosphere prevents oxidation in both types of furnaces.

ACKNOWLEDGMENTS

The authors wish to acknowledge their indebtedness to the Westinghouse Electric & Manufacturing Co. and to the Driver-Harris Co. for permission to publish the results. Helpful advice and encouragement were given by Messrs. P. H. Brace and H. D. McKinney. Many members of the Research staffs of both companies assisted in carrying out the tests and deserve a great deal of credit for the results of this paper. The authors wish further to thank Dr. C. H. Herty for his valuable suggestions regarding the application of his "aluminum method" for this work.

Some Metallurgical Characteristics of Induction Furnaces as Determined by the Absorption of Oxygen by Molten Nickel*

By F. R. Hensel,† Pittsburgh, Pa., and J. A. Scott,‡ Harrison, N. J.

(New York Meeting, February, 1932)

Abstract

The paper deals with the investigation of two types of coreless induction furnaces, one of 60 cycles, the other of 5000 cycles. Nickel was used as test material and the absorption of oxygen by molten nickel was chosen for determining the influence of the frequency on the metallurgical characteristics of the furnaces. Dr. Herty's aluminum method, slightly modified, was found suitable for determining the nickel oxide content in nickel. Also an electrolytic method for determining alumina in nickel was worked out. The solubility-temperature relations for nickel oxide in molten nickel were determined approximately. It was found that the solubility of nickel oxide increases with the temperature. Comparative tests on the rate of oxygen absorption made in a 60 and a 5000-cycle furnace showed that the absorption of nickel oxide in nickel is an increasing function of turbulence, time and temperature. The rate of oxygen pickup in the 60-cycle furnace is about three times as great as in the 5000-cycle furnace. In the 60-cycle furnace the maximum oxygen content of the melt comes close to the saturation limit. Melting under an oxygen-free atmosphere prevents oxidation in both types of furnaces.

DISCUSSION

(*Howard Scott presiding*)

H. Scott, East Pittsburgh, Pa.—When Professor Desch was in Pittsburgh recently he mentioned that the induction furnace has practically replaced the crucible furnace in Sheffield except for the carbon tool steels. Dr. Hensel is to be congratulated on the development of analytical methods for determining inclusions and for getting two different methods to agree.

F. R. Hensel.—Recently the purification of molten metals with hydrogen or other suitable gases has become an important issue and a number of patents have been taken out covering gaseous treatments of molten metals. In this connection I wish to call attention to the possibilities of the 60-cycle furnace as a melting tool. The possibility of gaseous treatments of molten metals ever becoming practical depends entirely upon its economy. The economy of a metallurgical process is determined by the rate of the metallurgical reactions. As shown in this paper, the rate of these reactions in a 60-cycle furnace is approximately three or four times as great as in an ordinary high-frequency induction furnace, owing to the great turbulence of the 60-cycle furnace. Further, there would be no necessity for tuyeres in such a furnace. Blowing hydrogen, for instance, on top of the melt should be more efficient than tuyeres and should bring every particle of the melt in intimate contact with the gas.

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* This paper is available at the office of the Institute as a *Preprint*.

† Group Engineer, General Metallurgical Group, Westinghouse Research Laboratories.

‡ Driver-Harris Co.

The limitations in melting and finishing a charge in a 60-cycle furnace could be overcome by the development of a coreless induction furnace with a frequency range from 25 to 1000 cycles. Grid glow tubes or grid-controlled mercury arc rectifiers might be used for that purpose. Then melting down and finishing of the charge could be done at 1000 cycles while 25 to 60 cycles would be employed during the refining stages.

The fact that we found a considerable nitrogen absorption in air atmosphere and practically no nitrogen absorption under a pure nitrogen atmosphere seems to point to a peculiar mechanism of the nitrogen absorption by molten metals. I have studied this phenomenon carefully in connection with electric arc welding and hope to report my findings soon.

Copper Embrittlement, II

By L. L. Wyman,* Schenectady, N. Y.

(Buffalo Meeting, October, 1932)

Since the presentation, by the writer, of the initial paper on the embrittlement of copper,[1] the subject has been investigated further along two separate lines. The first series of investigations involves the "double-deoxidized" coppers, while the second series is devoted to single deoxidizers other than those used in the investigations reported upon last year.

The object of these experiments is to develop a type of copper that will show the minimum of detrimental effects after having been exposed to alternate oxidation and reduction. The fabrication of this material necessitates the use of alternate oxidizing and reducing atmospheres, at temperatures ranging up to 900° C. Following this treatment it is essential that the soundness and strength of the copper be unimpaired, even in sections of only a few thousandths of an inch in thickness.

MATERIALS

The ensuing report embodies three separate groups of materials, which may be classified as follows:

1. Double-deoxidized copper using silicon and calcium boride.
2. Copper deoxidized with calcium.
3. Double-deoxidized copper using constant calcium content (0.075 per cent) plus silicon, or calcium boride.

Last year, T. S. Fuller, of the General Electric Research Laboratory, suggested that if a properly deoxidized copper had sufficient deoxidizer residual in the material, this excess material might increase the resistance of the copper to the oxidation reduction cycle. In consequence of this suggestion, two small lots of "double-deoxidized" copper were prepared. The first, lot A, was made by adding 0.03 per cent silicon as the deoxidizer, following this by an addition of 0.55 per cent calcium boride immediately before pouring. The second, lot B, contained the same ingredients, but these were added in the reverse manner.

Inasmuch as these lots were tested separately from the materials about to be described, it must be borne in mind that the materials cannot be grouped together, and are not directly comparable.

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* Research Metallurgist, General Electric Co.

[1] L.L. Wyman: Copper Embrittlement. A.I.M.E. *Preprint* (1931).

The second and third groups of materials used in these experiments consist of single and double deoxidized copper, prepared by Mr. Zickrick,[2] all of which were made from the same base material. The copper used for the base metal of these alloys was a wire bar which contained 0.06 per cent oxygen, by analysis. After this copper had been remelted, it was found that the oxygen content, by analysis, was 0.028 per cent.

Inasmuch as silicon and calcium boride have been the most promising deoxidizers used in previous work, they have been used as the base materials for double deoxidization in the following experiments. Table 1 gives the additions that were made to these coppers, as well as the chemical analyses of the resulting alloys, the analyses being obtained through the courtesy of the American Brass Company.

TABLE 1.—*Additions to Coppers and Resulting Alloys*

Lot No.	Additions			Residual		
	Silicon	Calc. Boride	Calcium	Silicon	Calcium	Oxygen
A	0.03-1st	0.55-2d	0			
B	0.03-2d	0.55-1st	0			
1	0	0	0			0.028
2	0	0	0.0375		Trace	0.002
3	0	0	0.075		0.044	0
4	0	0	0.15		0.090	0
5	0	0	0.25		0.180	0
6	0.075	0	0		0.03	0
7	0.075-1st	0	0.075-2d	0.067	0.057	0
	Added	Together				
8	0.075	0	0.075	0.065	0.068	0
9	0	1% 150	0	0.007	Trace	0
10	0	5% 150-1st	0.075-2d	0.006	0.045	0

METHODS

The treatment accorded these alloys was the same as that reported in the author's earlier paper; namely:

1. Ingot samples were cold-rolled to 0.125 in. thick and annealed at temperatures from 400° to 900° C., at 100° C. intervals, for a period of 15 min. This is the "single-muffle" series.

2. The samples of the second series were subjected to the same temperatures for a period of 30 min. This is the "double-muffle" series.

3. After having been subjected to the muffle treatments, samples of each of the series were subjected to heat treatment in hydrogen furnaces at 500°, 650° and 800° C. The latter treatment was accomplished in a

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[2] L. Zickrick: Properties of Copper Deoxidized with Calcium. See page 152, this volume.

conventional type of hydrogen tube furnace equipped with a water cooler, into which the samples were pushed following the heat treatments.

Following the furnace treatments, the samples were mounted in fusible metal and prepared for microscopic examination. The first step in the examination consisted of etching the samples very lightly with dichromate-sulfuric acid etching reagent, and examining for oxide penetration. The second step consisted of etching further with chromic acid, to accentuate the "band," which shows the penetration of oxygen in these deoxidized materials. It has been the writer's experience that chromic acid will attack the band much more readily than the unaffected copper. A final examination was made to determine the depth of the "open-grain" structure.

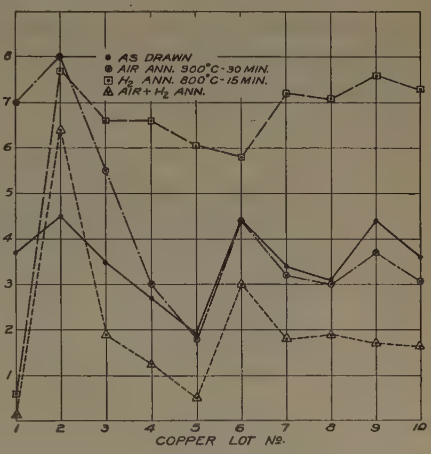


FIG. 1.—BEND TEST ON 0.045-IN. WIRE.

All of the samples were examined (1) as rolled, (2) after hydrogen treatments, (3) after muffle treatments, and (4) after muffle and hydrogen treatments. The microscopic examinations and measurements were made at a magnification of 250 diameters.

Where definite occurrences of copper oxide could not be seen, and particularly at penetrations deeper than the visible occurrences of copper oxide, the "band" was taken as the depth of penetration. In the calcium coppers, there was an absence of the band on the surface of the treated samples, but there occurred an intergranular separation which appeared to be a function of the heat treatment.

RESULTS

Because so many of the results fall very close together, the diagrammatic representation of these results by graphs is confusing; consequently these figures are tabulated. Table 2 shows the results of examination for total penetration of oxygen, as denoted by copper oxide and the band, as well as the penetration of the separated material in the calcium coppers. Table 3 gives the tabulated results of the measurements of the depth of the open-grain structure due to the blowing open of the structure during the hydrogen treatments.

With reference to the effect of these heat treatments on lots A and B, Table 4 shows the results of measurements of the depth of the open structure. These results are quite erratic, although the general trend indicates consistently low penetrations of the open-grained structure.

BEND TESTS

In addition to the results obtained from the oxidation-reduction tests on the 0.125-in. rolled stock, it was decided to supplement these tests by the regular bend tests, as recommended by the Bell Telephone Laboratory.

TABLE 2.—*Total Penetration of Oxygen*

MUFFLE TEMP / LOT No.		SINGLE MUFFLE						DOUBLE MUFFLE					
		400°C	500°C	600°C	700°C	800°C	900°C	400°C	500°C	600°C	700°C	800°C	900°C
1	500°C HYDROGEN	125	125	125	125	125	125	125	125	125	125	125	125
2		0	0	0	0	0	0	0	0	0	0	0	0
3		0	0	0	0	p3	p9	0	0	0	0	p4	p11
4		0	0	0	0	p2	p8	0	0	0	0	p3	p9
5		0	0	0	0	p1.5	p[illegible]	0	0	0	p1	p3	p6
6		0	0	0	b.5	b3	b7	0	0	b.5	b1	b4	b7
7		0	0	0	$\substack{b\\p}$.5	$\substack{b\\p}$2	$\substack{b\\p}$6	0	0	$\substack{b\\p}$.5	$\substack{b\\p}$.1	$\substack{b\\p}$2	$\substack{b\\p}$6.5
8		0	0	$\substack{b\\p}$.5	$\substack{b\\p}$.5	$\substack{b\\p}$1.5	$\substack{b\\p}$6.5	0	$\substack{b\\p}$.5	$\substack{b\\p}$.5	$\substack{b\\p}$1.5	$\substack{b\\p}$2	$\substack{b\\p}$7
9		0	0	0	b.5	b1.5	b8	0	0	0	b1.5	b2.5	b8.5
10		0	0	0	$\substack{b\\p}$.5	$\substack{b\\p}$2	$\substack{b\\p}$7	0	0	$\substack{b\\p}$.5	$\substack{b\\p}$1.5	$\substack{b\\p}$4	$\substack{b\\p}$8
1	650°C HYDROGEN	125	125	125	125	125	125	125	125	125	125	125	125
2		0	0	0	0	0	0	0	0	0	0	0	0
3		0	0	0	0	p4	p10.5	0	0	0	p1.5	p4.5	p11.5
4		0	0	0	0	p3	p8.5	0	0	0	p1	p3.5	p8.5
5		0	0	0	0	p2.5	p6.5	0	0	0	p1	p3	p6.5
6		0	0	0	b1	b3	b6.5	0	0	b.5	b1	b4.5	b7.5
7		0	0	0	$\substack{b\\p}$.5	$\substack{b\\p}$2	$\substack{b\\p}$6	0	0	$\substack{b\\p}$.5	$\substack{b\\p}$1	$\substack{b\\p}$2.5	$\substack{b\\p}$7.5
8		0	0	0	$\substack{b\\p}$1	$\substack{b\\p}$1.5	$\substack{b\\p}$6.5	0	0	0	$\substack{b\\p}$1	$\substack{b\\p}$2	$\substack{b\\p}$7
9		0	0	0	b1	b2.5	b8.5	0	0	b1	b1	b3	b9
10		0	0	$\substack{b\\p}$.5	$\substack{b\\p}$1	$\substack{b\\p}$3	$\substack{b\\p}$7	0	0	$\substack{b\\p}$1	$\substack{b\\p}$1	$\substack{b\\p}$3.5	$\substack{b\\p}$9
1	800°C HYDROGEN	125	125	125	125	125	125	125	125	125	125	125	125
2		0	0	0	0	0	0	0	0	0	0	0	0
3		0	0	0	0	p3.5	p11	0	0	0	p15	p4	p11
4		0	0	0	0	p2.5	p9	0	0	0	p1	p3	p95
5		0	0	0	0	p2	p6	0	0	0	p1	p2.5	p6.5
6		0	0	b.5	b1	b2.5	b7	0	0	b.5	b1	b4	b8.5
7		0	0	0	$\substack{b\\p}$1	$\substack{b\\p}$2.5	$\substack{b\\p}$8	0	0	$\substack{b\\p}$.5	$\substack{b\\p}$1	$\substack{b\\p}$2.5	$\substack{b\\p}$8
8		0	0	0	$\substack{b\\p}\frac{1}{2}$	$\substack{b\\p}$2.5	$\substack{b\\p}$7.5	0	0	0	$\substack{b\\p}$.5	$\substack{b\\p}$3	$\substack{b\\p}$8
9		0	0	b$\frac{1}{2}$	b1	b3	b9	0	0	b.5	b1	b3.5	b9.5
10		0	$\substack{b\\p}$.5	$\substack{b\\p}$1	$\substack{b\\p}$2	$\substack{b\\p}$2.5	$\substack{b\\p}$7	0	$\substack{b\\p}$.5	$\substack{b\\p}$1	$\substack{b\\p}$2	$\substack{b\\p}$3	$\substack{b\\p}$9

PENETRATIONS IN .001" p = GRAIN BOUNDARY SEGREGATE b = BAND

Ingot samples of the 10 experimental lots were drawn down to 0.045-in. wire, and bend tests were made on these wires over jaws having 0.1125-in. radius. These tests were made on wires (1) as drawn, (2) after air-annealing at 900° C. for 30 min., (3) after hydrogen annealing at 800° C. for 15 min., and (4) after annealing for 30 min. at 900° in air and 15 min. at 800° C. in hydrogen. The latter represents the maximum treatment accorded the rolled stock. Fig. 1 shows graphically the results of these bend tests.

INTERPRETATION

The results obtained from the first lots of double-deoxidized copper, lots A and B, seemed to substantiate the view that residual deoxidizer would increase the resistance to "blowing open" of the grains as the result of oxidation-reduction treatment.

TABLE 3.—*Depth of Open-grain Structure Due to Blowing Open of Structure During Hydrogen Treatments*

OPEN GRAINS

MUFFLE TEMP. / LOT No.		SINGLE MUFFLE						DOUBLE MUFFLE					
		400°C	500°C	600°C	700°C	800°C	900°C	400°C	500°C	600°C	700°C	800°C	900°C
1	500°C HYDROGEN	4	4	4	4	4	4	4	4	4	4	4	4
2		0	0	0	0	0	0	0	0	0	0	0	0
3		0	0	0	0	?	?	0	0	0	0	?	?
4		0	0	0	0	?	?	0	0	0	0	?	?
5		0	0	0	0	?	?	0	0	0	0	?	?
6		0	0	0	.5	3	7	0	0	.5	1	4	7
7		0	0	0	0	1	1	0	0	.5	1	1	1
8		0	0	.5	.5	1	1	0	0	.5	1	1	1
9		0	0	0	.5	1.5	2	0	0	0	0	1	2
10		0	0	0	.5	2	2	0	0	0	1	1^2	2^2
1	650°C HYDROGEN	20	21	20	27	28	26	20	20	21	26	28	28
2		0	0	0	0	0	0	0	0	0	0	0	0
3		0	0	0	0	?	?	0	0	0	0	?	?
4		0	0	0	0	?	?	0	0	0	0	?	?
5		0	0	0	0	?	?	0	0	0	0	?	?
6		0	0	0	1	3.5	7	0	0	.5	1	3.5	7.5
7		0	0	0	0	1.5	2.5	0	0	.5	1	1.5	2.5
8		0	0	.5	1	1	1.5	0	0	1	1	1.5	1.5
9		0	0	0	0	1	2	0	0	0	0	1	2.5
10		0	0	0	.5	1.5	2	0	0	.5	1	2	2.5
1	800°C HYDROGEN	625	625	62.5	625	625	625	62.5	625	62.5	625	625	625
2		0	0	0	0	0	0	0	0	0	0	0	0
3		0	0	0	0	?	?	0	0	0	0	?	?
4		0	0	0	0	?	?	0	0	0	0	?	?
5		0	0	0	0	?	?	0	0	0	0	?	?
6		0	0	0	1	3	7	0	0	.5	1	3.5	8
7		0	0	0	1	2	2.5	0	0	.5	1	2	2.5
8		0	0	0	1	15	2	0	0	.5	1	1.5	2.5
9		0	0	.5	1	1.5	2	0	0	.5	1	2	2
10		0	0	0	1	2	2.5	0	0	.5	1	2.5	2.5

penetrations in .001"

Following the attainment of these results, several large lots of this type of material were put into production. The results to date prove conclusively the superiority of the double-deoxidized material to a normal copper deoxidized by either of the component deoxidizers.

TABLE 4.—*Measurements of Depth of Open Structures*

Penetration in 0.001 Inch

Lot No.	Muffle Temp., Deg. C. in H_2	Single Muffle						Double Muffle					
		400° C.	500° C.	600° C.	700° C.	800° C.	900° C.	400° C.	500° C.	600° C.	700° C.	800° C.	900° C.
A	500	0	0.5	1	1	2	5	0	0.5	1	1	1.5	2
B		0	1	1	1.5	2	2.5	0	1	1	1	2	2.5
A	650	0	1	1	2	4	5	0.5	1	1.5	2	2	2.5
B		0	0	0.5	1	3	3.5	0	0	0.5	1	3	3.5
A	800	0.5	1	1.5	2	2	2	0.5	1	1	1.5	1.5	2
B		0.5	0.5	2	2	2	2	0.5	0.5	1	1	1.5	2

Sections of metal 0.006 in. thick have consistently remained sound and strong in production, showing that the experimental and factory results are in complete accord.

Table 4 shows that lot B is consistently more resistant than lot A; that is, the silicon added last gives a more resistant material.

As might well be anticipated, material excess silicon makes for increased trouble in the mechanical working of these materials. The production statistics verify not only the differences with respect to embrittlement, but also to the mechanical working of these two lots of copper.

In the series of calcium coppers, the copper that was used as the base metal responded in the anticipated manner to the tests, and the higher hydrogen treatments caused complete penetration of the "open" structure (Fig. 2).

As calcium is added to this material in increasingly larger amounts, several interesting factors appear. The addition of 0.0375 per cent calcium leaves a material in which only minute amounts of any disperse matter are visible (Fig. 3). As the calcium additions increase from 0.075 to 0.25 per cent there are increasing amounts of disperse material with increasing calcium. Fig. 4 shows the large amount present in lot 5. With the higher calcium additions some of this segregation also occurs intergranularly.

The hydrogen has caused no apparent effect on these calcium alloys, but the air, and air plus hydrogen, anneals cause a separation of a large amount of intergranular material between the surface grains in the alloys of higher calcium content.

Lot 2 seemed to be impervious to all treatments, whereas lot 3 gave a large amount of this intergranular segregation. Increasing the amounts of calcium did not, apparently, increase the depth of this separation but, on the contrary, the depth of separation decreased with increasing calcium.

It is also of interest that the calcium coppers were devoid of the band which usually characterizes the deoxidized coppers after treatment.

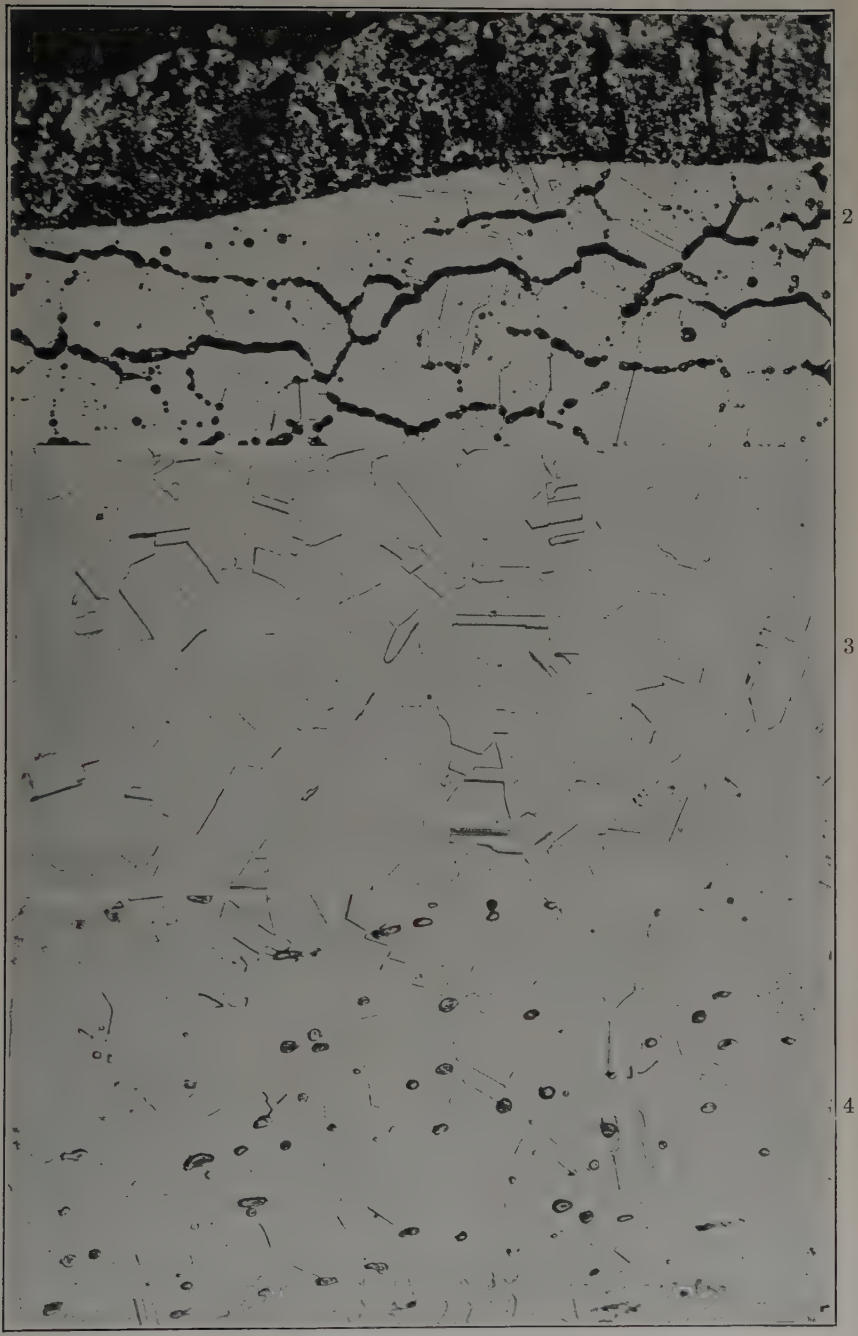
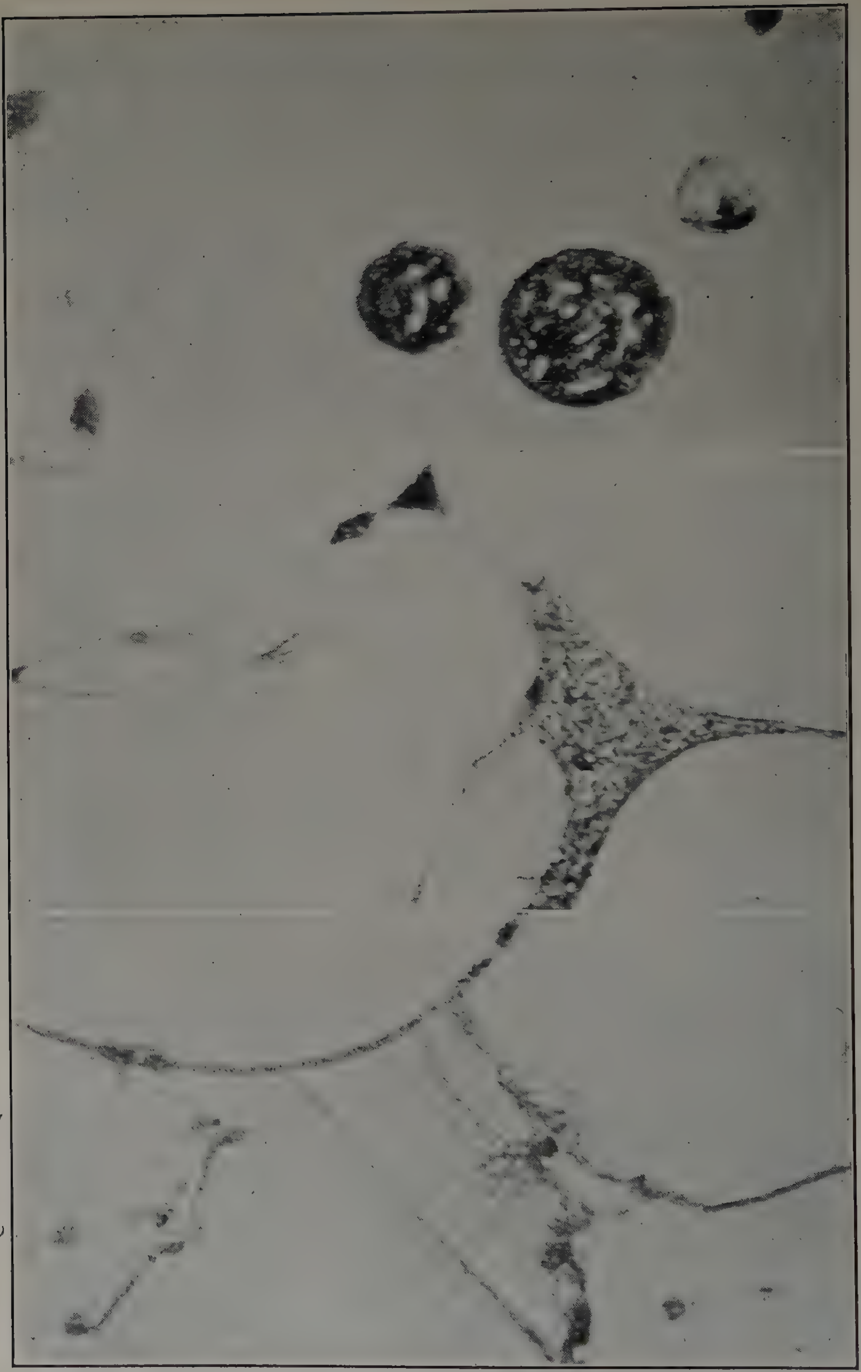


Fig. 2.—Copper base metal; 0.028 per cent oxygen.
Fig. 3.—Base metal with 0.0375 per cent calcium added.
Fig. 4.—Base metal with 0.25 per cent calcium added.
All × 250. $K_2Cr_2O_7$-H_2SO_4 etch.



Figs. 5 and 6.—Material dispersed throughout samples of lot 5.
Fig. 7.—Material from edge of lot 5.
All × 1500. $K_2Cr_2O_7$-H_2SO_4 etch.

Chromic acid as an etching reagent is extremely useful in this respect, as it attacks a band much more rapidly than it does unaffected copper. However, neither the chromic acid nor other usual etchants would develop a banded structure in this material.

An examination of the material which has separated at the boundaries in lots 3, 4 and 5 shows that this material is, apparently, of the same eutectiferous nature as the material dispersed throughout these samples. Figs. 5 and 6 taken from lot 5, and Fig. 7 from the edge of lot 5, substantiate this view. These photomicrographs show the complex nature of this separated material, whether it occurs as dispersed globules throughout the body of the copper, or in the grain boundaries.

From the work of Baar,[3] which seems to be generally accepted, there appears to be no solubility of calcium in copper. It is more than probable, however, that there is a very small solubility, but inasmuch as only small amounts are being considered, any solubility whatsoever would readily account for this intergranular segregation at the surface. The excess calcium would necessarily occur as a eutectic; which amply accounts for the appearance of this segregate. It is doubtful whether these materials are identical in composition, even though their structures are similar.

The addition of 0.0375 per cent calcium has left the copper unharmed after the oxidation-reduction cycle, indicating very favorable resistance to this test. The other samples of calcium copper show no evidences of open grain structure, and do not appear to be very much influenced by a hydrogen anneal, either in forming this segregate or in opening up, as substantiated by the bend tests. However, when the air-annealed, and air-plus-hydrogen-annealed samples are bend-tested, it is found that the separation at the boundaries has occurred, and that the bend-test results have fallen lower with increasing calcium.

It would seem logical to conclude that the lowered bend-test values caused by large calcium addition, or by the double deoxidation wherein the calcium could be residual, as noted below, are due primarily to the intergranular segregation and not to opening of the grains or embrittlement of the structure by "gassing." This interpretation is substantiated by the work of Schumacher, Ellis, and Eckel.[4]

The third group of copper samples shows the influence of double deoxidation. Silicon and calcium boride are used in conjunction with a constant amount of calcium. The individual performances of the former are shown in lots 6 and 9. The double deoxidation effect is determined by adding 0.075 per cent calcium to the materials deoxidized with silicon and calcium boride.

Lot 6 is a material that has been treated with the usual amount of silicon, and its reaction to the tests is the same as found in the better grades of this material reported previously.[5] When this is changed to a "double-deoxidized" copper by the final addition of 0.075 per cent calcium, lot 7, there is a decided increase in its resistance to the oxidation-reduction treatments. The addition has materially increased the bend values after the hydrogen anneal, but has also greatly decreased these same values for all other anneals. The simultaneous addition of the same amounts of these materials shows, if anything, a slightly improved material as regards the oxidation-reduction tests, and slightly poorer values in the bend tests.

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[3] Baar: *Ztsch. f. anorg. Chem.* (1911) **70,** 352.

[4] Schumacher, Ellis, and Eckel: *Trans.* A.I.M.E. (1930) **89,** Inst. Metals Div., 151.

Lot 9 has been deoxidized with a very large amount of calcium boride reagent, and the much improved performance over lots previously tested[5] is probably due to this large addition.

Lot 10 has only one-half as much reagent added as had lot 9 (as much as frequently used), but has, in addition, 0.075 per cent calcium. The calcium was added last. This material shows but slight improvement over the copper single deoxidized with calcium boride. On the other hand, when it is considered that in the double-deoxidized sample only slightly over one-half as much deoxidizer has been added, the result may be interpreted favorably. The bend tests, however, reflect the double addition, as mentioned before.

The "residual" columns of Table 1 give rise to some points of considerable interest.

Concerning lot 2, it is noted that the loss in calcium is close to the total amount added, 0.0375 per cent, but there is a trace remaining. Furthermore, there is 0.002 per cent oxygen present. It would thus appear that this material is very close to a completely deoxidized copper having a minimum of residual deoxidant.

Theorizing on the beneficial effects of residual deoxidant, this material would not appear to be very resistant to the tests applied. The writer has at different times tested commercial materials which are reported to fulfill this characterization of having neither residual oxygen nor deoxidizer. Experience with such material under the tests applied here have invariably shown that a section 0.125 in. thick will be completely blown open under the maximum test conditions.

It can only be opined that calcium is an extremely active deoxidant, and that only traceable amounts can afford a protective action toward these tests. In the higher calcium additions, each of these lost approximately one-half of the calcium added.

These alloys stand up well against the oxidation-reduction tests, but their strength is lowered by intergranular segregation near the surface. This may be interpreted as being actuated by the conditions of the tests but must not be confused with the embrittlement caused by oxygen-reducing gas effects.

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[5] Reference of footnote 1.

When silicon is used as a deoxidant, over one-half of the added amount is lost. When this same amount of silicon is supplemented by either a second or simultaneous addition of calcium, the losses in deoxidants are materially decreased and the performance is improved.

The calcium boride alloys are of interest because nearly all of the added material is eliminated. Lot 3, having 0.075 per cent calcium added, shows a residual 0.044 per cent of this material, whereas lot 10, with a like addition, supplementing the calcium boride, retains 0.045 per cent calcium. This verifies the results on lot 9, where 1 per cent calcium boride retained but a trace of calcium.

Considering the test results, it is evident that the additions of calcium as a supplementary deoxidant have improved the performances of the calcium boride and silicon-deoxidized coppers. However, when these double-deoxidized coppers utilizing 0.075 per cent calcium are compared to lot 3, of like calcium addition, it is clear that the initial addition of these other deoxidants has decreased the effectiveness of the calcium.

Conclusions

The interpretation of the results of the foregoing experiments lead definitely to the conclusions that:

1. The addition of calcium in small amounts, as represented by lot 2, gives superior qualities as regards resistance to embrittlement.
2. Excessive calcium additions prove detrimental to the physical properties (bend test) of copper, corroborating the work of Schumacher, Ellis and Eckel,[6] and of Zickrick.[7]
3. None of the calcium coppers appear to be detrimentally affected by the usual copper embrittlement; that is, the "gassing" or blowing open of the grain boundaries.
4. In all of the lots tested, the double deoxidizing has proved superior to single deoxidation, for similar or larger amounts of the same deoxidants. Lot 2 may be considered an exception to this statement.

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[6] Schumacher, Ellis and Eckel: Reference of footnote 4.

[7] Reference of footnote 2.

[For discussion see page 162.]

Properties of Copper Deoxidized with Calcium

By Lyall Zickrick,* Schenectady, N. Y.

(Buffalo Meeting, October, 1932)

Experiments of previous investigations have indicated that calcium-copper alloy, when used as a deoxidizer for molten copper, results in a sound copper casting of good physical and electrical properties. Bradenberg and Wiens[1] have obtained successful results in casting sound copper using calcium for deoxidizing. Masing[2] has obtained deoxidized copper of high density and high conductivity by use of calcium. Pratt,[3] in 1907, patented the use of calcium for the deoxidation and degasification of copper. Schumacher, Ellis and Eckel,[4] in 1929, conducted a series of experiments on deoxidizing copper with calcium. They concluded that so long as there is only a small percentage of residual calcium the mechanical and electrical properties of the copper deoxidized are not impaired, and the deoxidation is thorough.

For this investigation, a copper-calcium alloy high in calcium and 10 variously deoxidized copper ingots were prepared. The investigation concerns itself with the casting properties and structure of these variously deoxidized ingots, their working and annealing characteristics, and the resulting physical and electrical properties of the worked materials.

Preparation of Special Copper-calcium Alloy and Experimental Ingots

For use as a deoxidizing agent, an alloy of copper and calcium with fairly high calcium content was prepared, by melting pure electrolytic copper in a graphite crucible in an ordinary gas-fired pot furnace. The molten copper was kept well covered with calcium chloride slag. Small chunks of calcium were wrapped in thin copper sheet, placed on the end of a graphite rod and plunged down into the molten copper and thoroughly stirred. Upon completion of the calcium additions the crucible content was poured out into a cake about one inch thick. Analysis of this alloy gave 4.4 per cent calcium. The alloy was brittle and easily broken into small chunks. Some calcium was lost during the addition, owing to burning. The molten copper was held at a temperature of about 1200° C. and the calcium added as expeditiously as possible.

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* Metallurgist, General Electric Co.

[1] Brandenberg and Wiens: *Eng. & Min. Jnl.* (1906) **82,** 433.

[2] Masing: *Wiss. Veroffen. a. d. Siemens-Konzern* (1928) **7,** 321.

[3] Pratt: Deoxidation of Copper. Brit. Pat. 1699 (1907).

[4] Schumacher, Ellis and Eckel: *Trans.* A.I.M.E. (1930) **89,** Inst. Metals Div., 151.

For a supply of high-oxygen copper to use in manufacturing these ingots a special wire bar was obtained which analyzed 0.06 per cent oxygen. This bar was cut into pieces weighing about 10 lb. each, and one piece was used in the making of each ingot.

All melting was done in a gas-fired pot furnace using a graphite crucible, and the copper charges were all kept covered with an equal amount of charcoal so as to eliminate as much variation as possible in the melting procedure. The gas flame was regulated in the same manner and equal periods of time were taken to melt. The calculated amount of deoxidizer, wrapped in copper foil, was added and stirred into the charge with a graphite rod just before pouring. The charges were cast in a graphite mold into rods of 1¼-in. diameter, weighing about 5 lb. each.

DEOXIDIZERS USED

The first ingot was prepared without the addition of any deoxidizer to determine the effect of the established melting procedure upon the oxygen content of the copper. To heats 2 to 5 inclusive were added increasing amounts of the copper-calcium alloy, melt No. 6 received the usual percentage of silicon-copper deoxidizer, and melts 7 and 8 each received like amounts of calcium and silicon. In preparing melt No. 7 the silicon alloy was stirred in first, and followed with addition of the

TABLE 1.—*Melts and Deoxidizers*

Melt No.	Deoxidizer Added, Per Cent	Deoxidizing Element Remaining in Metal, Per Cent	Copper + Silver	Oxygen	Sulfur
1			99.968	0.028	0.0017
2	Ca, 0.0375	Trace	99.972	0.002	0.0002
3	Ca, 0.075	Ca, 0.044	99.929	nil	0.0001
4	Ca, 0.150	Ca, 0.090	99.859	nil	0.0001
5	Ca, 0.250	Ca, 0.180	99.786	nil	0.0000
6	Si, 0.075	Si, 0.03	99.925	nil	0.0003
7	Si, 0.075 Ca, 0.075	Si, 0.067 Ca, 0.057	99.869	nil	0.0000
8	Si, 0.075 Ca, 0.075	Si, 0.065 Ca, 0.068	99.856	nil	0.0000
9	CaB_6 reagent,[a] 1.0	Si, 0.007 Ca, Trace	99.920	nil	0.0001
10	CaB_6 reagent,[a] 0.5 Ca, 0.075	Si, 0.006 Ca, 0.045	99.903	nil	0.0000

[a] Calcium boride reagent is reported as containing 3 to 6 per cent carbon, 0.5 per cent silicon and the remainder calcium boride (CaB_6).

calcium alloy. In preparing melt No. 8 the silicon and calcium alloys were wrapped and added together. Melt 9 was deoxidized with calcium boride reagent and melt 10 was deoxidized with calcium boride, followed by copper-calcium alloy. The various melts and deoxidizers used are as shown in Table 1. A certain amount of the deoxidizing agent is used to deoxidize, combining as an oxide and slagging off; the remainder tends to remain in the metal as a mechanical mixture or to enter into solid solution. Samples taken from the ingots for analysis gave results as shown in Table 1. For comparison, the addition percentages are also listed.

The large and excess additions of calcium to melts 3, 4 and 5 were made to afford a means of determining the effect of residual calcium, and enable one to draw a comparison between this effect and the effect of residual silicon remaining in melt 6.

Casting Characteristics of Ingots

The ingots as cast show the more or less well developed pipe characteristic of deoxidized copper. A well developed shrinkage cavity is to a degree indicative of well deoxidized and gas-free copper. The top 4 in. of each ingot has been sectioned longitudinally to show the pipe. These are illustrated in Fig. 1. Ingot No. 1 shows a very small shrinkage cavity and small holes due to entrapped gas which failed to escape. Traces of silica were discernable on the exterior and in the pipe of ingot 6, which was deoxidized with silicon.

Oxygen and Sulfur Content of Ingots

Chemical analyses for oxygen, sulfur and copper plus silver were performed for us by C. H. Davis at the laboratories of the American Brass Co. The results of these determinations are as shown in Table 1. The method used was indirect; that is, the oxygen was calculated by taking the loss in weight of the sample after it was subjected to the hydrogen treatment.

Microstructure of Ingots

The microstructure of the cast ingots may be seen in Figs. 2 and 3. According to Baar[5] the solubility of calcium in copper is extremely small. The copper-calcium equilibrium diagram as published by Baar appears in Fig. 4. A eutectic between copper and calcium occurs at 910° C. and contains 5.7 per cent calcium. In Fig. 2, the No. 1 ingot, to which no deoxidizer had been added, shows the presence of copper-oxide eutectic. In ingots 2, 3, 4 and 5 to which increasing amounts of calcium were added,

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[5] Baar: *Ztsch. f. anorg. Chem.* (1911) **70,** 352.

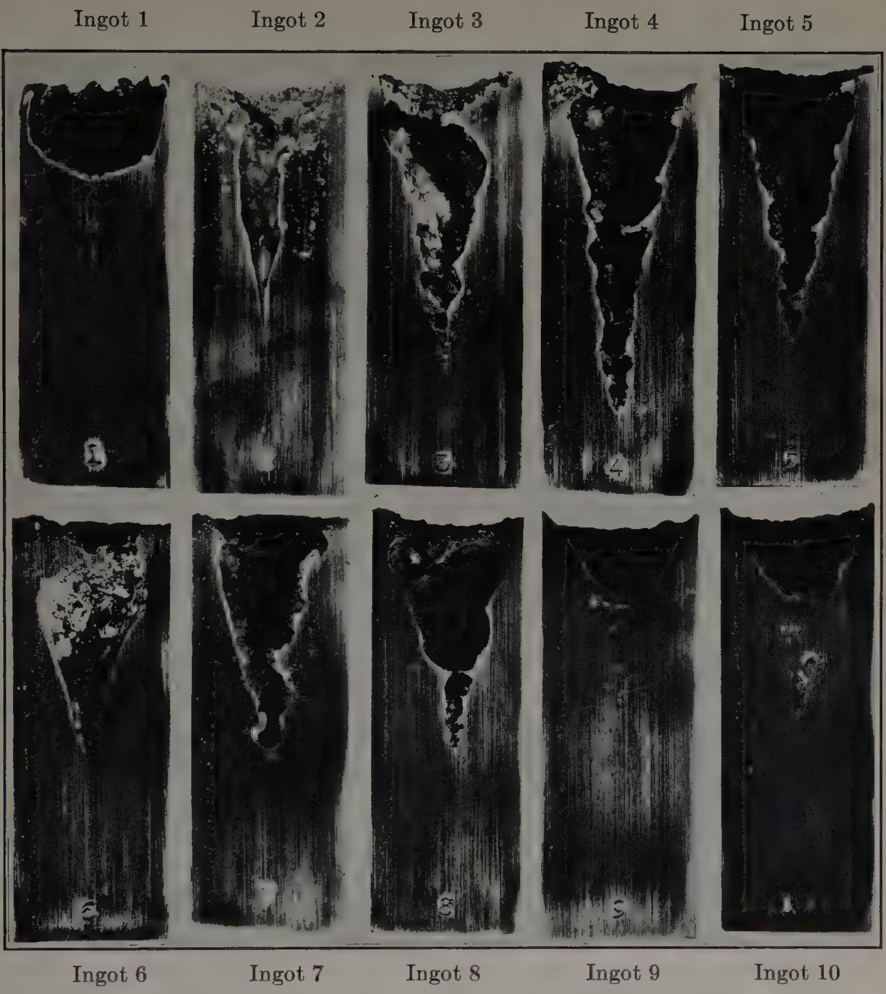

Fig. 1.—Pipes obtained in ingots deoxidized with various reagents.

Reagent, Per Cent
No. 1.—None
No. 2.—0.0375 Ca
No. 3.—0.075 Ca
No. 4.—0.15 Ca
No. 5.—0.25 Ca

Reagent, Per Cent
No. 6.—0.075 Si
No. 7.—0.075 Si + 0.075 Ca
No. 8.—0.075 Si + 0.075 Ca
No. 9.—1.0 CaB_6 reagent
No. 10.—0.5 CaB_6 reagent
0.075 Ca

Fig. 2.—Deoxidized copper ingots, showing effect of various deoxidizers. × 200 (Reduced ½; original magnification given.)

Deoxidizers, Per Cent
No. 1.—None
No. 2.—0.0375 Ca
No. 3.—0.075 Ca
No. 4.—0.15 Ca
No. 5.—0.25 Ca
No. 6.—0.075 Si

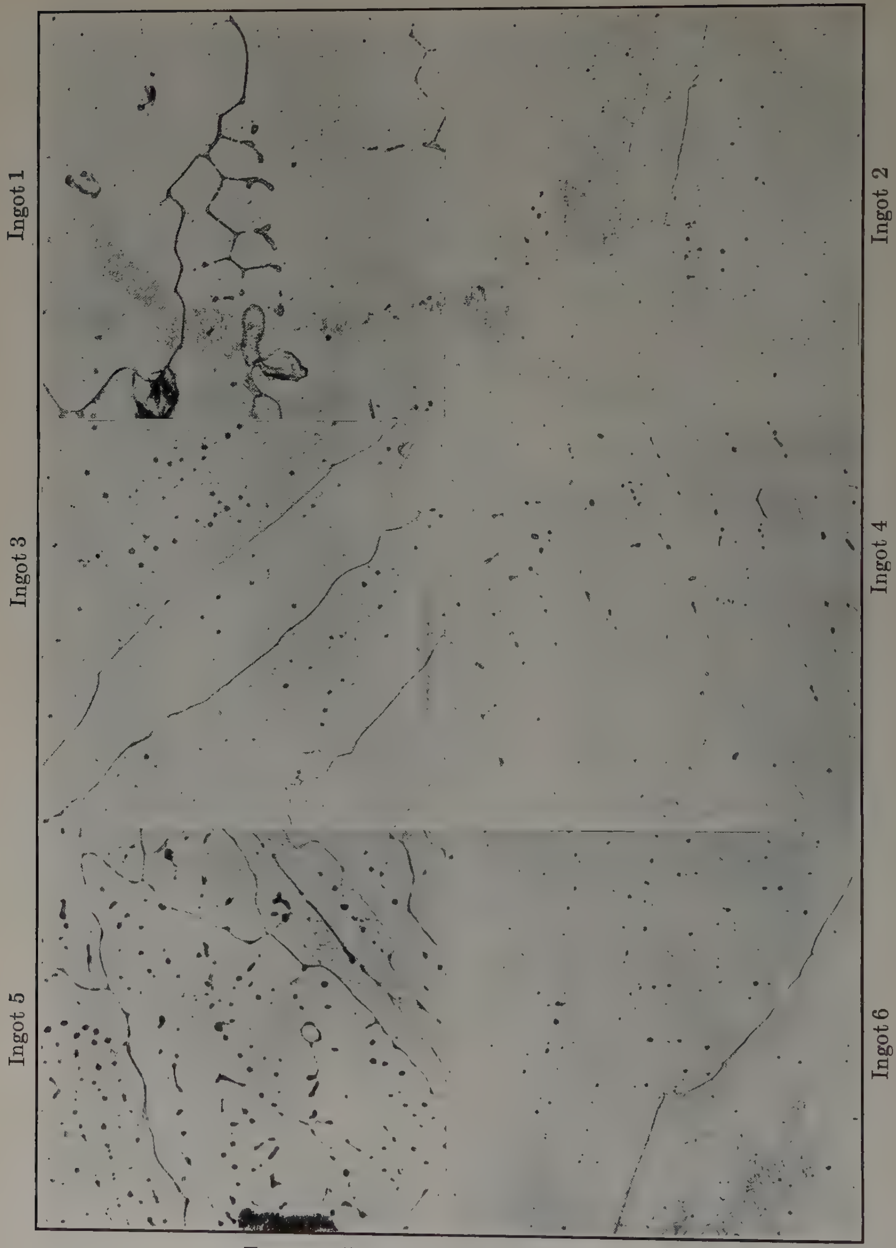

FIG. 2.—CAPTIONS ON OPPOSITE PAGE.

the calcium constituent shows up as small dark particles. These particles at a magnification of 1500 show eutectic structure. They show a marked increase in number as the calcium content increases, and in ingot 5, to which 0.25 per cent calcium was added, the particles are of larger size and some of the constituent also appears in the grain boundaries.

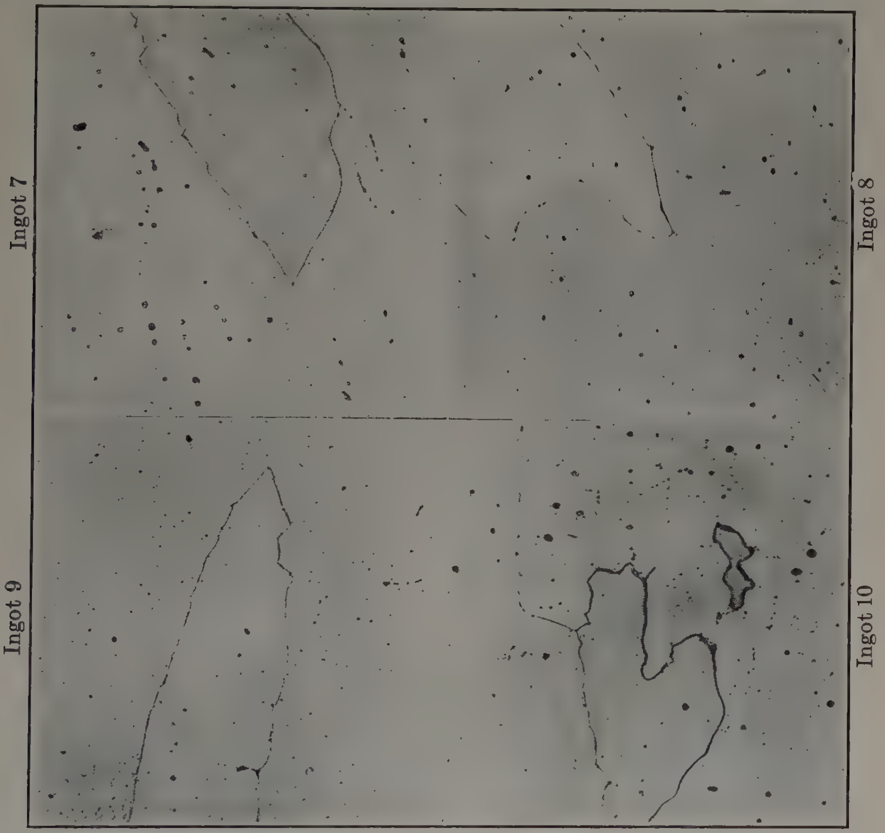

FIG. 3.—DEOXIDIZED COPPER INGOTS SHOWING EFFECT OF VARIOUS DEOXIDIZERS. × 200. (Reduced ½; original magnification given.)

DEOXIDIZERS, PER CENT

No. 7.—0.075 Si + 0.075 Ca
No. 8.—0.075 Si + 0.075 Ca
No. 9.—1.0 CaB_6 reagent
No. 10.—0.5 CaB_6 reagent
0.075 Ca

FABRICATION AND ANNEALING

All 10 ingots were successfully swaged to rod of 0.25 in. diameter, annealed, then drawn without any further anneal to wire of 0.045 in. diameter. Considerable care had to be exercised in swaging the high-calcium ingots, No. 4 and especially No. 5, so that they should not be swaged at too high a temperature. Baar, in his diagram for copper-calcium alloys, shows a second eutectic point at 560° C. and approximately 38 per cent of calcium. Ingots 4 and 5 when swaged at this temperature showed a tendency to crack and exhibited indications of containing a constituent of low melting point. As soon as the ingots cooled to below 400° C. they swaged without any additional trouble. It seems reasonable to believe that in the cast condition there may be an amount of the calcium present as the 560° C. eutectic.

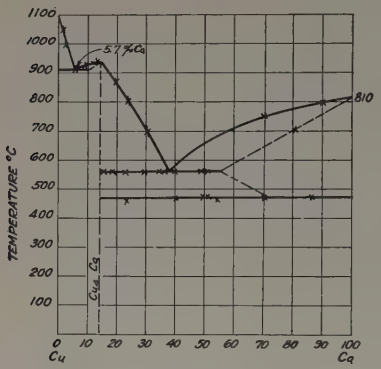

FIG. 4.—COPPER-CALCIUM EQUILIBRIUM DIAGRAM BY BAAR.

Small coils of the 0.045-in. wires were annealed in a bath of Crisco for 6 and for 15-min. periods at 200°, 250°, 300°, 350° C. and in a high-temperature oven at 400° C. Coils were also annealed in a muffle furnace for 30 min. at 700° C., and 30 min. at 700° C. followed by a 15-min. anneal in hydrogen at 800° C. These heat-treated wires were then tested on a Louis Schopper testing machine for tensile strength and percentage of elongation, and on a double Kelvin bridge for percentage of conductivity.

TENSILE STRENGTH, ELONGATION, AND CONDUCTIVITY DATA ON ANNEALED WIRES

Tables 2 and 3 give the summary of the results of the various physical and electrical data.

TABLE 2.—*Tensile Strength and Elongation*

All Samples Annealed for a Period of 6 Minutes

Anneal, Deg. C.	Sample 1		Sample 2		Sample 3		Sample 4		Sample 5	
	Tens. Str.[a]	Elong.[b]	Tens. Str.[a]	Elong.[b]	Tens. Str.[a]	Elong.[b]	Tens. Str.[a]	Elong.[b]	Tens. Str.[a]	Elong.[b]
H.D.	62,300	1.2	65,200	1.3	66,850	1.4	67,450	1.2	67,600	1.3
200	45,370	10.6	60,130	2.4	63,470	1.4	66,150	2.1	68,150	1.9
250	36,700	35.2	45,000	10.7	57,700	2.9	63,350	2.1	62,300	1.8
300	36,350	37.3	37,200	30.3	43,050	19.4	47,600	7.8	54,600	3.0
350	36,350	35.6	37,350	34.6	37,700	33.3	39,000	28.3	40,850	25.1
400	36,250	37.4	36,850	34.0	37,000	32.1	38,300	32.9	39,350	29.8
Spec.[c]	20,530	5.1	36,800	29.4	36,700	29.6	38,550	29.1	38,800	26.3

Anneal, Deg. C.	Sample 6		Sample 7		Sample 8		Sample 9		Sample 10	
	Tens. Str.[a]	Elong.[b]	Tens. Str.[a]	Elong.[b]	Tens. Str.[a]	Elong.[b]	Tens. Str.[a]	Elong.[b]	Tens. Str.[a]	Elong.[b]
H.D.	68,900	1.3	68,650	1.2	70,000	1.5	66,400	1.8	66,750	1.4
200	65,650	1.9	66,850	1.6	68,450	1.6	60,500	1.6	64,900	1.5
250	62,050	2.2	63,900	1.2	64,750	2.1	48,050	10.1	58,600	2.9
300	44,050	9.5	50,250	5.6	52,500	4.7	37,250	23.9	42,000	17.7
350	36,450	29.9	38,000	29.4	38,550	29.7	37,300	34.5	37,500	33.3
400	36,400	30.3	37,200	34.1	37,250	29.5	37,150	35.9	37,500	35.3
Spec.[c]	39,250	22.8	36,800	26.6	37,200	27.3	37,300	31.3	38,000	29.6

[a] Tensile strength, lb. per sq. in. [b] Elongation, per cent in 10 in.

[c] Annealed 700° C. in air 30 min., followed by 15 min. in hydrogen at 800° C.

TABLE 3.—*Conductivity Data*

All Samples Annealed for a Period of 15 Minutes

Sample No.	Anneal Treatment	Conductivity	Deoxidizer Added, Per Cent	Deoxidizer Remaining, Per Cent
1	H.D.	100.1		
	200	101.8		
	250	101.8		
	300	101.5		
	400	101.6		
2	H.D.	98.7	Ca, 0.0375	Trace
	200	99.3		
	250	100.5		
	300	101.1		
	400	100.7		
3	H.D.	95.1	Ca, 0.075	Ca, 0.044
	200	95.3		
	250	95.7		
	300	96.7		
	350	97.2		
	400	97.3		
4	H.D.	89.9	Ca, 0.150	Ca, 0.090
	200	90.1		
	250	90.3		
	300	91.7		
	350	91.6		
	400	91.7		
5	H.D.	82.7	Ca, 0.250	Ca, 0.180
	200	84.1		
	250	84.9		
	300	85.1		
	350	85.7		
	400	86.1		
6	H.D.	73.9	Si, 0.075	Si, 0.03
	200	73.9		
	250	74.2		
	300	75.1		
	350	75.2		
	400	74.9		
7	H.D.	72.4	Si, 0.075 Ca, 0.075	Si, 0.067 Ca, 0.057
	200	73.3		
	300	73.8		
	400	73.8		
8	H.D	70.4	Si, 0.075 Ca, 0.075	Si, 0.065 Ca, 0.068
	200	71.2		
	300	71.8		
	400	71.3		
9	H.D.	95.0	CaB_6, 1.0	Si, 0.007 Ca, Trace
	200	95.2		
	250	96.4		
	300	96.6		
	350	97.0		
	400	96.9		
10	H.D.	90.9	CaB_6, 0.5 Ca, 0.075	Si, 0.006 Ca, 0.045
	200	91.3		
	300	93.0		
	350	93.0		
	400	92.0		

REVIEW OF DATA OBTAINED

The effect of increasing amounts of residual calcium upon the annealing temperature required to produce a given percentage of elongation may be seen in Fig. 5. The wire from ingot 5 deoxidized with 0.25 per cent calcium and containing 0.18 per cent residual calcium in the metal requires a temperature of at least 400° C. to approach a complete anneal, whereas samples from ingot No. 1 (copper containing oxygen to which no deoxidizer has been added) fully anneal at temperatures of 250° to 275° C. For comparative purposes the elongation curve for wire from ingot 6 has been included and appears dotted in Fig. 5. This metal was deoxidized with 0.075 per cent silicon and contains 0.03 per cent residual silicon. That amount (0.03 per cent) of residual silicon is as effective in raising the annealing temperature of copper as is 0.10 to 0.20 per cent residual calcium, due to the fact that silicon enters into solid solution in the copper, in contrast to calcium, which is very slightly soluble.

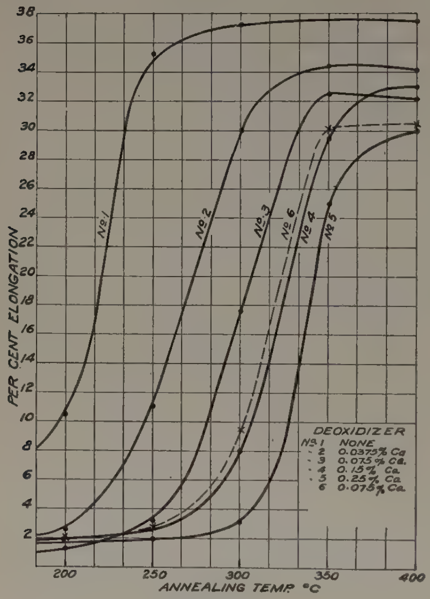

FIG. 5.

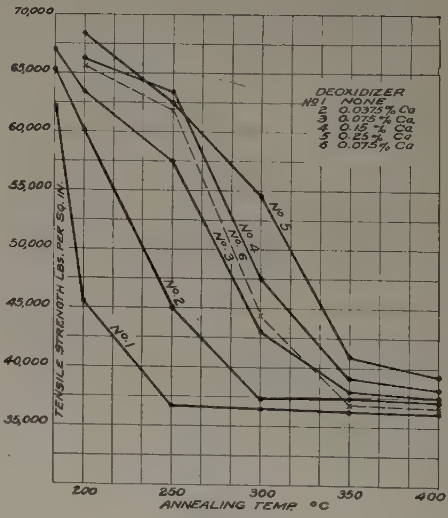

FIG. 6.

FIG. 5.—ELONGATION OF 0.045-IN. DIAMETER WIRE OBTAINED OF ANNEALING FOR 6 MIN. AT EACH TEMPERATURE INDICATED.

FIG. 6.—TENSILE STRENGTH OF 0.045-IN. DIAMETER WIRE OBTAINED BY ANNEALING FOR 6 MIN. AT EACH TEMPERATURE INDICATED.

In Fig. 6 have been plotted the tensile strengths for different annealing temperatures. The effect of calcium and silicon on the tensile properties for various annealing temperatures is essentially the same as its effect on elongation.

In Fig. 7, percentage of elongation has been plotted against percentage of calcium addition and each curve represents a different annealing temperature. The curve illustrates the marked effect of residual deoxidizer, remaining in the metal, on the annealing characteristics at the lower annealing temperatures. At the higher annealing temperatures the effect of residual calcium and silicon is not so noticeable.

Fig. 8 illustrates the effect of residual calcium and silicon on the electrical conductivity of wire, from ingots 1 to 5 inclusive, deoxidized with calcium, and ingot 6 deoxidized with silicon. Owing to the ability of silicon to enter into solid solution with copper, the effect of any remaining silicon on the electrical conductivity is very marked. Fig. 8 and Table 3 show that 0.03 per cent residual silicon drops the electrical conductivity to approximately 75 per cent that of pure annealed copper. The effect of residual calcium on the electrical conductivity is by no means so detrimental as silicon, the presence of approximately 0.03 per cent residual calcium depressing the conductivity to approximately 97 per cent, or only about a 3 per cent decrease. Increased amounts of residual calcium cause a further gradual decrease in conductivity, but by no means so great a decrease as is produced by silicon. Calcium not entering into solid solution in the copper to any marked extent does not in turn materially affect its electrical properties. The drop in conductivity which does take place is due undoubtedly to the presence of the eutectic that occurs as dark particles within the grains, as may be seen in ingots 2, 3 and 4 on Fig. 2 and to some extent in the grain boundaries as in No. 5.

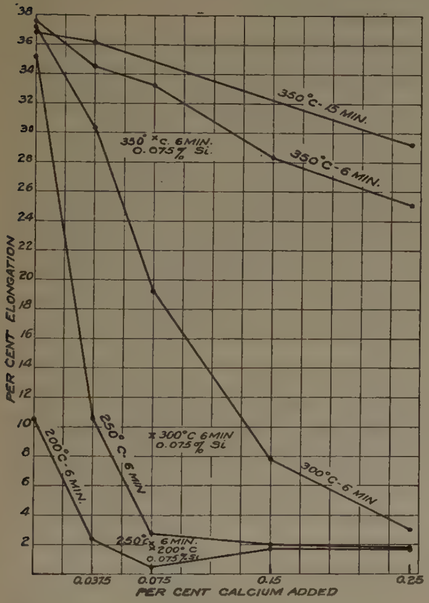

FIG. 7.

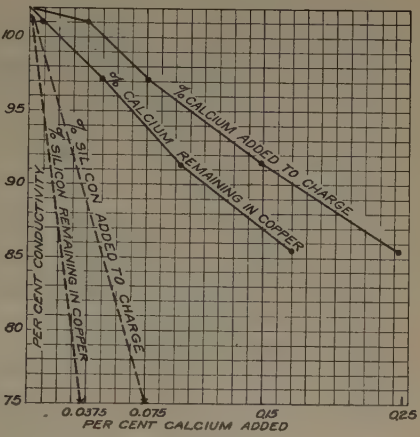

FIG. 8.

FIG. 7.—INFLUENCE OF VARYING PERCENTAGES OF CALCIUM ON ANNEALING CHARACTERISTICS OF COPPER WIRE.

FIG. 8.—EFFECT OF CALCIUM AND SILICON ON CONDUCTIVITY OF ANNEALED COPPER WIRE.

Annealing wires from the 10 lots first in air at 700° C. followed by an anneal in hydrogen at 800° C. showed the characteristic embrittlement due to combination of hydrogen with oxygen in samples from sample 1 (not deoxidized). None of the other samples showed any indication of embrittlement.

SUMMARY

A high-calcium copper alloy has been found to deoxidize copper satisfactorily.

Residual calcium remaining in the metal, like residual silicon, raises the annealing temperature required to produce dead soft copper. As small an amount as 0.05 per cent residual calcium raises the annealing temperature of copper from 250° to approximately 350° C., and when calcium is present in amounts up to 0.20 per cent, the required annealing temperature is in the neighborhood of 400° C.

Owing to the very slight solubility of calcium in copper in the solid state, residual calcium does not decrease the electrical conductivity of copper as silicon does. For a specific illustration it was found that 0.03 per cent residual calcium dropped the conductivity of dead soft copper from 101 to 97 per cent, while 0.03 per cent residual silicon caused a drop of from 101 to 75 per cent.

L. L. Wyman has taken samples from the 10 ingots described here and has conducted an investigation of their microstructure and oxygen content as affected by the oxidation-reduction treatment.[6] This treatment is essentially an anneal in an oxidizing atmosphere at 900° C. followed by an anneal in hydrogen at 800° C.

ACKNOWLEDGMENTS

The author wishes to express his appreciation to Mr. Charles Schmid and Mr. C. H. Davis of the American Brass Co. for their kind services in assisting with the physical tests and the chemical analyses.

DISCUSSION

[This discussion refers also to the paper by L. L. Wyman, which begins on page 141.

(*Sam Tour presiding*)

E. E. Schumacher, New York, N. Y. (written discussion).—Some time ago, at Bell Telephone Laboratories, we made a study of the deoxidation of copper with various metallic deoxidizers and reported our data in several publications.[7] Since

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[6] L. L. Wyman: Copper Embrittlement, II. See page 141.

[7] E. E. Schumacher, W. C. Ellis and J. F. Eckel: Deoxidation of Copper with Calcium and Properties of Some Copper-calcium Alloys. *Trans.* A.I.M.E. (1930) **89**, Inst. Met. Div., 151–161.

E. E. Schumacher, W. C. Ellis and J. F. Eckel: The Deoxidation of Copper with the Metallic Deoxidizers, Zinc, Beryllium, Barium. Strontium, and Lithium. *Metals*

Mr. Zickrick's paper deals with the same subject, naturally we are much interested in it.

The data in Table 3 show, as is to be expected, a progressive lowering of the conductivity with increasing amounts of calcium remaining in the melt. The values of conductivity, however, are all lower than those obtained by us in our investigation. For instance, we found that residual calcium to the extent of 0.18 per cent lowered the conductivity of the annealed wire to about 97.5 per cent, whereas Mr. Zickrick reports a conductivity of only 86.1 per cent for an alloy of the same composition. This greater lowering of the conductivity may be the result of impurities that were picked up from the refractory by the copper during the melting procedure, something that, unless extreme precautions are observed, can easily take place in the presence of an active reducing agent. By using alundum-lined graphite crucibles, as we did, it is possible to obtain deoxidized copper practically free from impurities save for any excess deoxidizer that remains in the melt. Mr. Zickrick reports that his alloys were melted in a graphite crucible. It has been our experience that copper melted and reduced in an ordinary clay-graphite crucible picks up appreciable quantities of silicon and aluminum owing to the interaction of the reducing agent with the materials of the crucible. We would be interested to know more about the type of crucible used by Mr. Zickrick; also, whether he had his samples analyzed for elements other than those mentioned in Table 1.

In a recent German publication,[8] Burkhardt and Sachs claim that lithium is definitely superior to calcium as a deoxidizer of copper. Any one, I think, who has worked with the metallic deoxidizers is willing to admit that lithium is a splendid deoxidizer. Under our conditions we find, however, that calcium functions more satisfactorily. Our experience is that the lithium, because of its great affinity for oxygen, attacks the refractory oxides of the crucible much more readily than does calcium. If real precautions are not taken to prevent this attack, sufficient quantities of metals will be liberated and alloyed with the copper to ruin it as a high-conductivity material. With conditions different from ours it is easily conceivable that lithium might function satisfactorily. Our belief, based on recent experience, is that a combination such as lithium with calcium, lithium with calcium boride, or calcium with calcium boride will prove to be more desirable as a deoxidizer for copper than any single metallic element, especially if high-conductivity copper is the ultimate objective.

D. L. Ogden, Carteret, N. J.—The conductivities obtained by Mr. Zickrick with calcium and calcium boride were lower than those obtained in commercial tests made at the plant of the United States Metals Refining Co. We were able to obtain conductivities on annealed No. 12 wire of 100.5 to 101 per cent in both cases. We found, however, that unless extreme care was taken, iron was absorbed from the refractories, which in the deoxidized state caused a decided drop in conductivity. The values obtained corresponded closely to the data given by Heuer.[9] We had several cases where the deoxidized copper contained 0.03 per cent iron with a conductivity around 95 per cent, while with the same iron content, copper having 0.005 oxygen had a conductivity of 100.6 per cent. It is evident that in deoxidized copper the iron is in solid solution with the copper and consequently has a more marked effect on the

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& Alloys (1930) **1,** 714–716.

E. E. Schumacher, W. C. Ellis and J. F. Eckel: The Deoxidation of Copper with the Metallic Deoxidizers, Calcium, Zinc, Beryllium, Barium, Strontium and Lithium. *Trans.* Electrochem. Soc. (1932) **61,** 91–99.

[8] Burkhardt and Sachs: *Metallwirtschaft* (April 22, 1932).

[9] R. P. Heuer: *Jnl.* Amer. Chem. Soc. (1927) **49,** 2711.

conductivity. It is possible that Mr. Zickrick's results have been influenced more by the impurities absorbed from his crucible than by the excess of reagent. We have also found in the case of calcium boride that impurities in certain lots of this reagent affected our final product.

We noted with interest that in swaging down the test bars for drawing at 560° C., the bars cracked. We had a similar experience with calcium-deoxidized copper. Vertical cast bars were being rolled in one of the local mills to ¼-in. rod. The first bar, rolled at the usual temperature, around 1500° F., broke into a number of pieces, showing the exact crystal structure of the casting and enabling us to pick out individual crystals of copper for study. The remaining bars were dropped in temperature to around 1200° to 1250° F. and gave satisfactory results.

D. K. Crampton, Waterbury, Conn.—We can confirm the general findings reported by Messrs. Schumacher and Ogden with regard to the importance of impurities reduced from furnace linings and other sources. We have found in a considerable amount of experimental work on deoxidized copper that appreciable quantities of silicon, aluminum and iron are ordinarily picked up. The silicon and aluminum probably come mainly from the refractories and the iron perhaps more from steel skimmers, iron strainers, and iron molds. The effect of all these elements on conductivity is marked. Iron in particular is one of the most troublesome elements to contend with.

We have done a considerable amount of work with calcium and lithium alloys for such deoxidation, in cooperation with Dr. Osborg of Maywood Chemical Co., and have obtained excellent results commercially. Recently we cast six 1000-lb. heats of copper from an Ajax-Wyatt furnace, all of which were deoxidized with an alloy of 50 per cent cadmium and 50 per cent lithium. Samples for conductivity were taken from the first and last part of the heats poured, making 12 conductivity determinations in all. The lowest conductivity obtained was 100.9 per cent and the average of the 12 determinations 101.5. These consistent and excellent results show what can be obtained with such a deoxidizing reagent, provided proper care is taken to avoid contamination as referred to above.

W. H. Bassett, Waterbury, Conn.—We can verify what has been said about the effect of iron from deoxidizing agents having done considerable work in this connection. No doubt deoxidizers reduce iron from refractories and iron from the various tools and refractories with which the copper comes in contact is responsible for low conductivity. Silicon and iron from calcium boride react to the detriment of conductivity.

E. R. Darby, Detroit, Mich.—We have used calcium very successfully with certain high-strength bronzes subject to heat treatment. Where the residual calcium is of the order of 0.01 per cent, a strength of 100,000 lb. can be secured, but where the residual calcium is higher than 0.03 per cent, a reduction of strength has resulted amounting to approximately 20 per cent.

T. A. Wright, New York, N. Y.—We chemists are complimented by the complacent way metallurgists often accept our results. However, those of us who have occasion often to check the work of others or study the effects of small percentages of added elements or impurities present are not quite so sure of some of the analytical procedures. Sincere and conscientious analysts get anomalous results due to analytical limitations.

Thus the determination of calcium in amounts equivalent to less than 0.10 per cent may be low on the one hand owing to incomplete precipitation of that element, while if silicon is also present in amounts of a hundredth or so incomplete precipitation of that metal may operate to counterbalance the calcium loss through co-precipitation. The analyses as given in the paper show quite a gap when totaled. Aside from the iron content as mentioned by others, is it not also possible that improved practice might disclose boron in cases where calcium boride had been added?

Perhaps Dr. Schumacher's comment on the lack of correlation between conductivity despite apparent concordance of the calcium figure may be explained in part by the possibility of one series of calcium determinations being low owing to incomplete precipitation of the calcium and the analyses of the other laboratory high because of co-precipitation of the silicon not previously removed. Such analytical phenomena, while not always appreciated as they should be, are not so rare as some people think. It would appear that the spectrograph could well be employed in such cases.

L. L. Wyman (written discussion).—I am pleased to hear Dr. Schumacher's statements regarding his experiences with "double deoxidized" copper, which clearly corroborate our own experiences. In using these alloys, which contain such minute amounts of alloying elements, we are really entering a new field. Most metallurgists and chemists are cognizant of the fact that we can no longer rely upon the older constitution diagrams of alloy systems for our guidance when dealing with these small quantities. Also, is it not true that many of our present chemical methods are equally antiquated, in this light, and that our future endeavors must involve studies of the effects produced by additions of minute amounts of alloying elements and the precise determinations of the amounts of these materials actually reacting? In the light of our present knowledge, we can at best but say that "under the conditions prevailing," such are the results.

L. Zickrick (written discussion).—Since the presentation of this paper, check analyses for calcium content of sample 5 have been performed by our laboratory and, through the courtesy of Mr. Ogden, by the laboratory of the United States Metals Refining Co. Our laboratory reports 0.19 per cent calcium as against 0.18 per cent previously. Mr. Ogden's laboratory reports 0.18 per cent calcium in sample A; 0.19 per cent calcium in sample B. Spectrograph analysis showed nothing but calcium, except a slight indication of iron. A wet analysis for iron of a 5-gram sample gave only a slight precipitate and the laboratory analyst reported the iron content as less than 0.001 per cent.

Comparative Properties of Oxygen-free High-conductivity, Phosphorized and Tough-pitch Coppers

By W. R. Webster,* J. L. Christie,† and R. S. Pratt,‡ Bridgeport, Conn.

(New York Meeting, February, 1933)

Since the delivery of our paper on Some Comparative Properties of Tough-pitch and Phosphorized Copper,[1] a new brand known as "oxygen-free high-conductivity copper" (brand OFHC) has become available to consumers. It was thought desirable to make a comparison between the properties of this material and those of the materials covered by our original paper and its discussion.

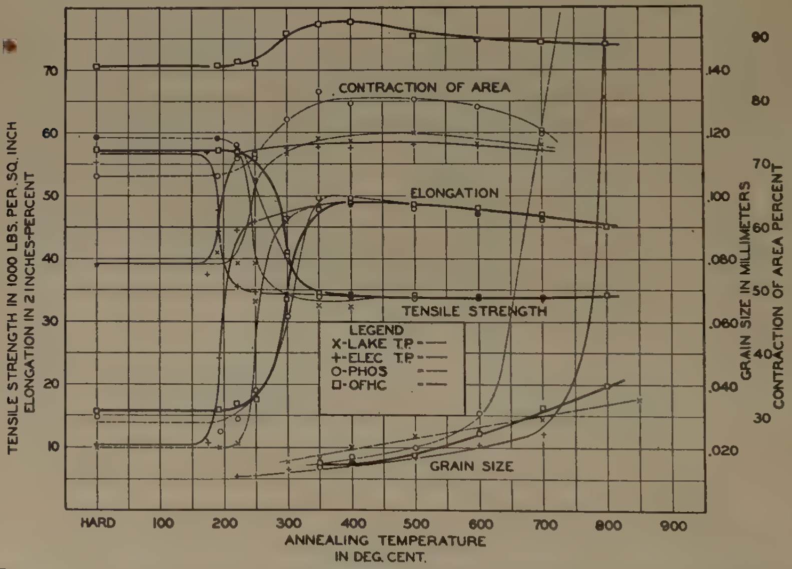

Fig. 1.—Characteristic annealing curves of various types of copper.

Preliminary tests had indicated some notable differences. A billet of oxygen-free high-conductivity copper was taken from regular production. A chemical analysis of the particular billet was not made, but the producer of the material has given as typical the analysis shown in Table 1. The billet was processed in accordance with the plan already adopted.[2] In addition, one billet each of copper deoxidized by calcium and by barium were submitted to us by a metallurgist of repute, but without details of the methods employed in making them. Portions of these billets were made into test pieces by following the same procedure as that employed in preparing all of the others and were tested.

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* Chairman of the Board, Bridgeport Brass Co.

† Metallurgist, Bridgeport Brass Co.

‡ Metallurgical Dept., Bridgeport Brass Co.

[1] *Proc.* Inst. Metals Div., A. I. M. E. (1927) 233.

Table 1.—*Typical Analysis of Oxygen-free High-conductivity Copper*

	Per Cent		Per Cent
Antimony	0.0028	Phosphorus	0.0000
Arsenic	0.0008	Selenium	0.0020
Bismuth	trace	Silicon	0.0015
Chromium	0.0000	Silver	0.002
Iron	0.0015	Sulfur	0.0025
Lead	0.0004	Tellurium	0.0011
Nickel	0.0016	Copper	99.98
Oxygen	0.0000[a]		
		Total	99.9962

[a] Oxygen not visible under the microscope at 200 diameters and not measurable by the ordinary laboratory methods.

Fig. 1 shows the effect of annealing on the tensile strength, elongation, contraction of area and crystal size of four kinds of copper: oxygen-free high-conductivity, tough-pitch electrolytic, tough-pitch Lake and phosphorized electrolytic. The curves for phosphorized electrolytic and tough-pitch Lake copper are those already published in our earlier paper; those for tough-pitch electrolytic copper were drawn from data of which

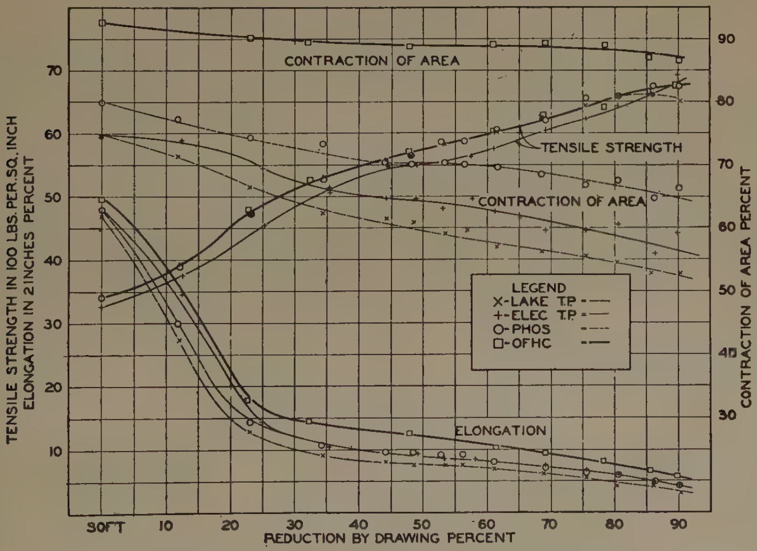

Fig. 2.—Characteristic drawing curves of various types of copper.

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[2] *Proc.* Inst. Metals Div., A. I. M. E. (1927) 248.

some were given in the authors' reply to the discussion of that paper; those of oxygen-free copper are typical of several sets of curves made.

Similarly, Fig. 2 shows the effect of cold drawing on the tensile strength, elongation and contraction of area.

Oxygen-free copper and electrolytic tough-pitch are relatively pure coppers, while Lake and phosphorized copper are alloys. It is therefore somewhat surprising that the oxygen-free copper resembles the phosphorized electrolytic rather than the tough-pitch electrolytic in the annealing temperature at which softening starts, but that resemblance has been shown in repeated experiments. The shapes of the temperature-grain size curves of phosphorized electrolytic and oxygen-free high-conductivity copper are worthy of note. It is recognized that for any given material the shapes of the curves can be changed by varying the treatment prior to annealing. In the experiments under discussion the previous treatments of all the coppers were the same, and so the apparent difference in the temperature at which rapid grain growth occurs is due to differences in the character of the coppers.

TABLE 2.—*Loss in Weight in Annealing, Quenching and Pickling*[a]
Grams per Square Inch of Surface

Temperature, Deg. C.	Total Loss in Weight in Annealing and Pickling			Loss in Weight in Quenching			Loss in Weight in Quenching, Percentage of Total Loss		
	OFHC	Phos. Elec.	Tough-pitch Elec.	OFHC	Phos. Elec.	Tough-pitch Elec.	OFHC	Phos. Elec.	Tough-pitch Elec.
500	0.027	0.017	0.029	0.019	0.015	0.022	70.4	88.2	75.8
600	0.053	0.041	0.051	0.044	0.032	0.048	83.0	78.1	94.1
700	0.076	0.095	0.071	0.043	0.091	0.065	56.6	95.8	91.5
800	0.226	0.185	0.151	−0.015[b]	0.159	0.021	0.0	85.8	13.9
900	0.362	0.367	0.359	−0.006[b]	0.300	−0.034[b]	0.0	81.7	0.0

[a] Samples consisted of tubing 1¾ in. O.D. by 0.156-in. wall by 1 in. long. They were annealed in muffle at indicated temperatures for ½ hour.

[b] Indicates an increase in weight.

On the drawing curves the high values for contraction of area and the flatness of the curve for oxygen-free copper are outstanding. It is recognized that phosphorized copper is much better suited for the manufacture of small seamless tubes than is tough-pitch copper. It was demonstrated in our earlier paper that the difference in properties of the two can be shown best by the position and slope of the contraction of area curves. On this basis, while confirmatory evidence is lacking as yet, it would appear that oxygen-free high-conductivity copper is capable of withstanding more severe drawing operations and a greater number of consecutive operations than even the phosphorized copper.

The tests on the copper deoxidized with calcium and on the copper deoxidized with barium gave results approximating those obtained from phosphorized electrolytic rather than oxygen-free high-conductivity copper. Because we are not sufficiently familiar with the properties of copper deoxidized with calcium and barium, we do not know whether the figures can be considered typical; therefore do not record them here.

It has been noted in processing oxygen-free high-conductivity copper that annealing scale tends to adhere to the metal, as it does with tough-pitch copper, instead of flaking off, as from phosphorized copper. Scaling experiments similar to those reported in our earlier paper were repeated, using tough-pitch electrolytic, phosphorized electrolytic and oxygen-free high-conductivity copper. In addition, after quenching, the samples were pickled to remove all the oxide formed. Figures on loss in weight are given in Table 2, showing that the total amount of oxide formed at a given temperature was about the same for all three kinds of copper. The figures also show that quenching removes very little scale from oxygen-free high-conductivity copper and tough-pitch electrolytic copper after annealing above 700° C.

DISCUSSION

(Albert J. Phillips presiding)

W. B. Price, Waterbury, Conn. (written discussion).—The authors make the following statement: "On this basis, while confirmatory evidence is lacking as yet, it would appear that oxygen-free high-conductivity copper is capable of withstanding more severe drawing operations and a greater number of consecutive operations than even the phosphorized copper." Our experience in drawing tubes of 3/8 in. outside diameter with a 0.005-in. wall thickness, drawn from 0.018-in. wall thickness to the finished wall thickness of 0.005 in., may be of interest. We used both phosphorized copper and oxygen-free high-conductivity copper and found that we had to use the same number of anneals between the redraws with both grades of copper. Seven redraws in all were used. This material was used soft and an additional forming operation was then carried out on the tube. We attempted to eliminate one or two anneals but found that with such thin material the metal would not stand the forming operation. However, for such articles as hard-drawn shells, for pencil tips, we would agree with the authors' statement as given above, that the oxygen-free high-conductivity copper would require fewer anneals than the phosphorized copper, and it might even be possible to draw these shells with six redraws without any process annealing.

W. R. Webster (written discussion).—We have found it perfectly practicable to draw oxygen-free copper tube from 0.542 in. by 0.0185 in. to 0.375 in. by 0.005 in. in five draws and two anneals, the initial reduction being 35 per cent and the final 19 per cent. In operations of this character, however, there are other factors involved than the mere ability of the material to withstand the reductions.

Fabrication and Properties of Seamless Phosphorized Arsenical Copper Tubing*

By G. L. Craig,† Columbus, Ohio, and O. Z. Klopsch,‡ Detroit, Mich.

(New York Meeting, February, 1933)

Abstract

The fabrication characteristics and properties of phosphorized arsenical Lake copper have been compared with phosphorized prime Lake and phosphorized electrolytic seamless copper tubing, in a series of mill-scale tests employing commercial drawing schedules. Phosphorized arsenical coppers containing as much as 0.20 per cent arsenic were drawn with various reductions into ⅞ and ⅜-in. seamless tubing along with billets of the two types of arsenic-free copper. The effect of arsenic was determined by the average power required to draw given compositions and by the final properties of the respective materials in the annealed condition and after various degrees of cold reduction. Power consumption data show that no more power is required to draw arsenical coppers of this type than the arsenic-free copper. The results of tensile tests indicate that arsenic increases the strength of cold-drawn tubing somewhat, but has no measurable effect on the properties of annealed tubing; the ductility of the tubing as evidenced by the elongation and other prescribed tests is unaffected by 0.20 per cent arsenic.

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* This paper is available at the office of the Institute as *Contribution No.* 15.

† Metallurgical Engineer, Battelle Memorial Institute.

‡ Factory Manager, Wolverine Tube Co.

AMERICAN INSTITUTE OF MINING AND METALLURGICAL ENGINEERS
Contribution No. 15 (CLASS E, INSTITUTE OF METALS DIVISION), FEBRUARY, 1933

DISCUSSION OF THIS PAPER IS INVITED. It should preferably be presented in person at the New York Meeting, February, 1933, when an abstract of the paper will be read. If this is impossible, discussion in writing may be sent to the Editor, American Institute of Mining and Metallurgical Engineers, 29 West 39th Street, New York, N. Y., for presentation by the Secretary or other representative of its author. Unless special arrangement is made, the discussion of this paper will close April 1, 1933. Any discussion offered thereafter should preferably be in the form of a new paper.

Fabrication and Properties of Seamless Phosphorized Arsenical Copper Tubing

BY G. L. CRAIG,* COLUMBUS, OHIO, AND O. Z. KLOPSCH,† DETROIT, MICH.

(New York Meeting, February, 1933)

COPPER containing a small amount of arsenic has been used extensively abroad, and a number of reports, particularly those by English workers, have indicated that such copper is better suited for certain uses than high-conductivity copper.

Inasmuch as a large percentage of the copper fabricated is used for nonelectrical purposes where high conductivity is not at all essential, it has been suggested that arsenical copper might be at least as suitable as high-conductivity copper for many purposes. An investigation sponsored by the Calumet & Hecla Consolidated Copper Co. at Battelle Memorial Institute was therefore undertaken with the object of determining the effect of small amounts of arsenic (up to 0.75 per cent) on the properties of copper. In this work the effect of arsenic on the basic properties of tough-pitch and of phosphorized copper have been critically studied and many data collected from laboratory experiments which have been supplemented by mill-scale tests. The results of these tests, with coppers of the type referred to, in the annealed condition and after various degrees of reduction, show that the basic properties of copper are not greatly affected by small amounts of arsenic, an increase in strength being observed with increasing arsenic with no corresponding decrease in ductility.

It is well known that the evaluation of material for plastic deformation, on the basis of laboratory tests, may not be directly comparable with its performance in commercial operations. In order, therefore, to substantiate the data obtained at the Institute, the cooperation of the Wolverine Tube Co. was obtained for a series of production tests on the fabrication characteristics of phosphorized arsenical copper in the manufacture of seamless copper tubing. In these tests the behavior of the arsenical coppers was carefully observed in comparison with that of representative types of phosphorized arsenic-free copper, which were fabricated under the same conditions.

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* Metallurgical Engineer, Battelle Memorial Institute.

† Factory Manager, Wolverine Tube Co.

Printed in U. S. A.

FABRICATION OF TUBING

In the first series of tests, 50 billets of phosphorized Lake copper containing as much as 0.20 per cent arsenic and, for comparison, 10 billets of phosphorized electrolytic copper furnished by the Wolverine Tube Co., were fabricated into two sizes of seamless tubing; 7⁄8 by 0.065 in. and 3⁄8 by 0.028 in.[1] The analyses of the billets are shown in Table 1.

TABLE 1.—*Phosphorized Copper Billets for Seamless Tube Production*

Lot No.	Billet No.	Specific Gravity Corrected to 4° C.		Silver, Oz. Per Ton	Oxygen, Per Cent	Sulfur, Per Cent	Phosphorus, Per Cent	Arsenic, Per Cent
		A	B					
0	2674-1	8.85	8.85	9.10	0.002	0.0001	0.014	0.001
	-2		8.84	9.25	0.004	0.0007	0.026	0.001
	2683-A	8.85	8.86	9.00	0.006	0.0004	0.026	0.004
	-B	8.83	8.83	9.20	0.005	0.0007	0.032	0.004
	-C	8.86	8.85	9.15	0.006	0.0005	0.025	0.005
	-D		8.86	8.90	0.009	0.0005	0.026	0.004
1	2675-A	8.85	8.86	9.20	0.005	0.0005	0.019	0.055
	-B	8.84	8.85	9.00	0.005	0.0008	0.020	0.056
	-C	8.82	8.83	9.20	0.004	0.0004	0.018	0.055
	-D	8.87	8.86	9.20	0.006	0.0004	0.016	0.055
	2684-A	8.83	8.84	9.15	0.005	0.0015	0.022	0.059
2	2676-A	8.84	8.85	8.90	0.005	0.0010	0.022	0.102
	-B	8.82	8.83	9.20	0.005	0.0007	0.028	0.105
	-C	8.84	8.85	9.15	0.006	0.0007	0.013	0.100
	2685-A	8.81	8.86	9.10	0.008	0.0003	0.033	0.111
	-B	8.82	8.84	9.15	0.007	0.0001	0.027	0.114
3	2677-A		8.85	8.95	0.005	0.0008	0.028	0.171
	-C	8.85	8.86	9.00	0.006	0.0003	0.021	0.171
	-D	8.83	8.84	9.20	0.005	0.0005	0.025	0.171
	2684-B	8.84	8.85	9.15	0.005	0.0003	0.028	0.174
	-C	8.85	8.86	9.00	0.006	0.0006	0.029	0.177
	-D		8.83	8.90	0.005	0.0003	0.027	0.173
4	2678-A	8.85	8.85	9.35	0.005	0.0010	0.028	0.204
	-B	8.85	8.86	8.95	0.004	0.0003	0.029	0.202
	-C	8.83	8.84	8.95	0.006	0.0008	0.023	0.200
	-D	8.84	8.85	8.95	0.007	0.0007	0.025	0.203
	2685-C	8.84	8.85	8.95	0.006	0.0012	0.028	0.186
Regular (Electrolytic)		8.834			0.003	0.0005	0.030	0.0001

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[1] The first dimension represents the external diameter of the tubing and the second dimension the wall thickness. This convention is followed throughout.

The primary charge in the preparation of all compositions, with the exception of the electrolytic, consisted of prime Lake copper. Small ingots were melted in a 1-ton oil-fired reverberatory furnace. The charge was oxidized to remove traces of impurities and poled to the tough-pitch stage. For the arsenic-free billets, sufficient metal for casting one billet was tapped into a ladle, the requisite amount of phosphor-copper for deoxidation added and the billet cast. The arsenical billets were then prepared in the order of increasing arsenic content, by additions of metallic arsenic to the melt followed by phosphorizing and casting. The billets were cast into preheated cylindrical iron molds, which had been coated with a dressing of lard oil and graphite. After solidification the billets were removed from the molds and quenched in water.

Base tubes approximately 2 by 0.130 in. were formed from the billets following the regular production schedule used in this mill. In the forming operation no differences were observed in the behavior of the various lots. The base tubes were then drawn cold in the usual manner, the reduction in area per draw being approximately 30 per cent. The power required for each draw was determined by means of a recording wattmeter. A typical portion of a chart is shown in Fig. 1. After the second draw the tubing was annealed at 700° C.

The average net power required is shown in Table 2. Readings for the first draw indicated that the power required for drawing decreased as the arsenic content of the tubing increased; this is, however, unquestionably due to a variation in the size of the base tubes rather than to the composition of the material. On the third and subsequent draws any variation in power requirements was due solely to the composition of the tubing, as all lots were annealed after the second draw, and were drawn through the same dies. Care was taken to see that the order of drawing was not a function of the arsenic content. No difficulty was encountered in drawing any of the lots, and, as may be observed from the data in Table 2, as much as 0.20 per cent arsenic did not increase the power required.

As a more severe test of the working properties of copper, a different lot of tubes of phosphorized electrolytic copper and of phosphorized Lake copper containing 0.20 per cent arsenic and 0.018 per cent residual phosphorus were drawn from 2 by 0.130-in. base tubing to $\frac{3}{8}$ by 0.028-in. tubing without intermediate annealing, a total reduction of 95.7 per cent. No difficulty was encountered in drawing either group of tubes, and the net power required, shown in Table 2, indicated that within the limits of accuracy possible the same power was required for drawing the two classes of material.

The power requirements for each pass in drawing the electrolytic copper and the Lake copper containing 0.20 per cent arsenic both when annealed after the second pass and when not annealed are shown in Fig.

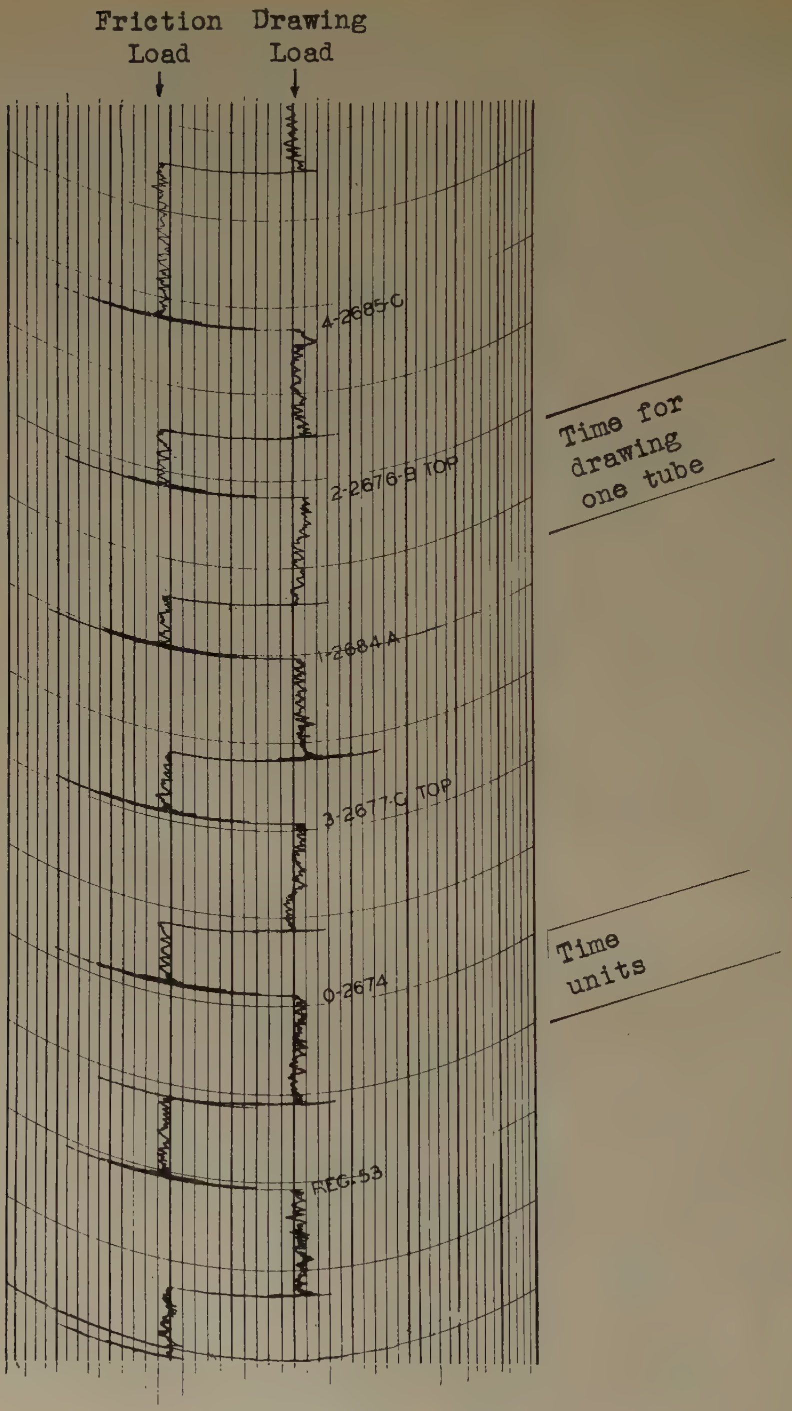

Fig. 1.—Power curves for all series, fourth draw.

2. From these data it is obvious that for drawing tubing no measurable increase in the power required results from the addition of 0.2 per cent arsenic to phosphorized copper.

MECHANICAL PROPERTIES OF TUBING

The properties of the following four types of tubing were studied: (1) base tubing, (2) annealed ⅞ by 0.065-in. tubing, (3) annealed ⅜ by 0.028-in. tubing prepared by annealing after the second draw, and (4) annealed and unannealed ⅜ by 0.028-in. tubing drawn without intermediate annealing. Tensile tests were made on annealed tubes with plugs inserted at both ends in order that the tubes could be firmly gripped in the testing machine.

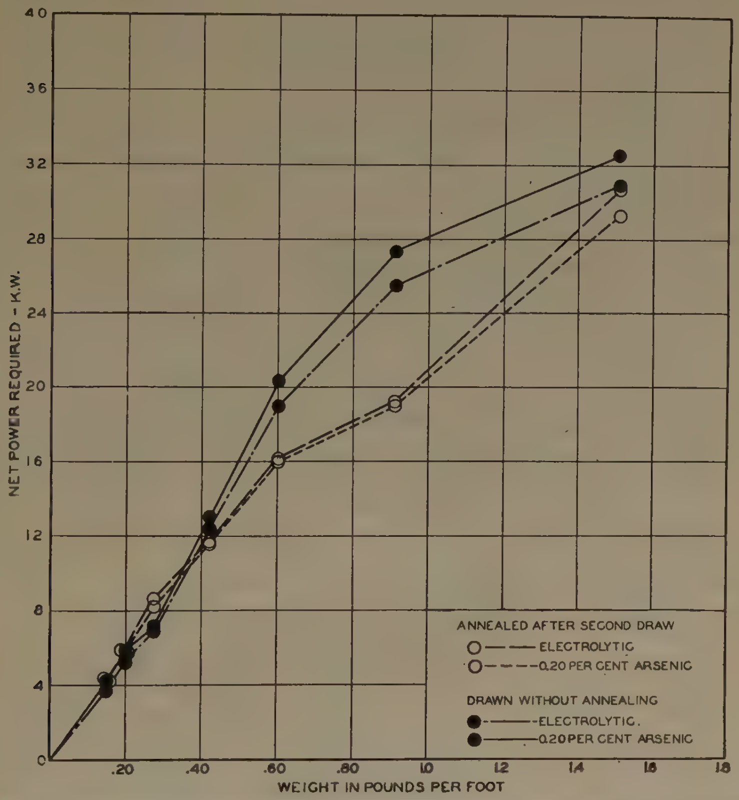

FIG. 2.—POWER-CONSUMPTION CURVES FOR ALL SERIES WITH AND WITHOUT INTERMEDIATE ANNEALING.

BASE TUBING AND ⅞ BY 0.065-IN. SERVICE TUBING

As nearly as could be determined by tensile and hardness tests on the base tubing, there was no difference between the properties of the arsenical and the nonarsenical tubing.

TABLE 2.—*Net Power Requirements for Drawing Various Compositions into Seamless Tubing*

Lot No.	Type	Power Requirements, Kw.[a]								
		Arsenic, Per Cent	1st Draw	2d Draw	3d Draw	4th Draw	5th Draw	6th Draw	7th Draw	8th Draw[b]
	ANNEALED AFTER SECOND DRAW									
Reg.	Commercial phosphorized electrolytic copper	0.0001	40.0	30.72	19.0	16.04	11.66	8.65	5.94	4.41
0	Phosphorized prime Lake copper	0.003	31.44	30.20	18.8	15.52	11.10	7.96	5.75	4.33
1	Phosphorized arsenical Lake copper	0.056	28.56	30.56	18.74	15.40	11.32	7.89	6.36	4.38
2	Phosphorized arsenical Lake copper	0.108	24.56	30.26	19.08	15.64	11.38	8.12	5.83	4.42
3	Phosphorized arsenical Lake copper	0.173	19.52	29.36	19.04	15.32	11.46	8.35	5.87	4.31
4	Phosphorized arsenical Lake copper	0.20	21.14	29.22	19.08	16.12	11.62	8.22	5.89	4.35
	DRAWN FROM BASE TUBE WITHOUT INTERMEDIATE ANNEAL									
	Commercial phosphorized electrolytic copper		28.92	30.88	25.5	19.0	12.4	6.90	5.22	3.70
	Phosphorized arsenical Lake copper	0.20	26.70	32.52	27.35	20.34	13.08	7.18	5.96	4.22

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[a] Average for 10 draws.

[b] ½ by 0.026 inch.

The ⅞ by 0.065-in. (¾ in. inside diameter) service tube was drawn from lengths cut from the base tubes after the second draw. The resulting lengths were annealed continuously at 700° C. The tubes were drawn from this size to the final size in two draws, the total reduction amounting to 30.6 per cent. The service tubes were coiled and bright-annealed at 700° C. for 1 hr. and had an average grain size of approximately 0.025 millimeters.

The tensile properties of the annealed tubing are shown in Table 3, where each value is an average obtained from six tests. As these data show, arsenic has no apparent effect on either the tensile strength or elongation.

Specimens of a length 1½ times the outside diameter (1⁵⁄₁₆ by ¾ in.) of the tubing under test were prepared from the same lengths and compositions used for the tensile tests, and were tested in compression following the procedure outlined in current A.S.T.M. standards. Duplicate samples from each tube were compressed by placing the specimens upright between the jaws of a testing machine, and applying the load gradually until the specimen had folded completely on itself as indicated by a sudden increase in load. All compositions were tested in this manner and in no single instance did cracks or other defects occur which might be indicative of failure. It is therefore concluded that all compositions in the series when fabricated and tested in the manner described will successfully pass such tests.

TABLE 3.—*Tensile Properties of Annealed ⅞ by 0.065-in. Service Tube*

Lot No.	Type	Tensile Strength, Lb. per Sq. In.[a]	Elongation, Per Cent[a]		
			2 In.	4 In.	8 In.
0	Phosphorized prime Lake	33,675	60.1	51.4	45.2
1	Phosphorized arsenical Lake, nominally 0.05 per cent As	32,775	58.4	48.7	42.7
2	Phosphorized arsenical Lake, nominally 0.10 per cent As	33,150	58.2	50.0	43.2
3	Phosphorized arsenical Lake, nominally 0.17 per cent As	34,000	58.7	50.4	43.9
4	Phosphorized arsenical Lake, nominally 0.20 per cent As	33,800	60.4	52.2	45.6
Reg.	Commercial phosphorized electrolytic copper	33,275	55.9	48.9	42.3

[a] Each value is the mean of six determinations.

Flaring tests were made on three specimens cut at random from tubes of each composition in the series, and from the same tubes from which the tensile specimens were taken. The specimens were 4 in. long, in accordance with specifications, allowing a sufficient length over the depth of the die block for the flange. The specimens were placed in the die block and formed by placing the whole assembly in the compression jaws of a tensile testing machine. After flaring the ram was raised and the cone replaced with a flattening tool. The ram was then lowered and the conical flange completely flattened on top of the die block. All compositions withstood the test equally well without the appearance of defects and without showing any indication of failure.

Three specimens, 1½ in. long, from each of the tubes on which the other reported tests were made, were flattened longitudinally by placing them in the compression jaws of a testing machine and applying the load until the specimens had been completely flattened. There was no evidence, in any of the compositions tested, of cracks or other types of defects indicative of failure.

In order to supplement the compression tests, opening tests were made on a series of two 3-in. specimens from each lot under test. The specimens were split and flattened completely without showing cracks or flaws.

⅜ BY 0.028-IN. TUBING

In the tubing produced by intermediate annealing after the second draw the total amount of cold reduction was approximately 87.1 per cent. This tubing was bright-annealed at 700° C. in a continuous furnace.

The results of tensile tests on this tubing are given in Table 4, where it will be observed that, like the ⅞ by 0.065-in. tubing, there is no real difference between the properties of the arsenical and the nonarsenical materials.

TABLE 4.—*Tensile Properties of Annealed ⅜ by 0.028-in. Seamless Copper Tubing*

Intermediate Anneal after Second Draw

Lot No.	Type	Tensile Strength, Lb. per Sq. In.[a]	Elongation, Per Cent[a]		
			2 In.	4 In.	8 In.
0	Phosphorized prime Lake	36,050	52.0	46.7	43.4
1	Phosphorized arsenical Lake, nominally 0.05 per cent As	36,300	52.3	46.0	42.1
2	Phosphorized arsenical Lake, nominally 0.10 per cent As	36,400	52.1	46.9	42.5
3	Phosphorized arsenical Lake, nominally 0.17 per cent As	36,000	54.0	48.1	43.4
4	Phosphorized arsenical Lake, nominally 0.20 per cent As	36,050	53.1	47.4	42.8
Reg.	Commercial phosphorized electrolytic copper	36,100	51.4	46.2	41.2

[a] Each value is the mean of five determinations.

TABLE 5.—*Tensile Properties* ⅜ *by* 0.028-*in. Seamless Copper Tubing*

Type	Tensile Strength, Lb. per Sq. In.[a]	Elongation, Per Cent[a]		
		2 In.	4 In.	8 In.
UNANNEALED. DRAWN FROM BASE SIZE WITHOUT ANNEALING. 96.5 PER CENT REDUCTION				
Phosphorized electrolytic copper	65,800	5.9	4.3	3.4
Phosphorized arsenical Lake copper	70,225	6.5	4.3	3.4
BRIGHT-ANNEALED. NO INTERMEDIATE ANNEAL				
Phosphorized electrolytic copper	35,325	52.7	46.9	43.0
Phosphorized arsenical Lake copper	36,550	54.2	48.6	43.2

[a] Each value is the mean of five determinations.

Hydrostatic tests were made on a series of representative samples of the ⅜ by 0.028-in. tubing and representative tubes from each composition withstood an internal hydrostatic pressure equivalent to a fiber stress of 6000 lb. per sq. in.

In the ⅜ by 0.028-in. tubing drawn without intermediate anneals the total reduction was 96.5 per cent. The tensile properties of both the annealed and unannealed materials are given in Table 5. According to these data, arsenic increases the strength of the unannealed tubing, but has no measurable effect on the tensile properties of the annealed tubing. By comparing these data with those given in Table 4 for the annealed tubing, it will be observed that practically no difference exists in the final properties of the two lots reduced 87 and 96.5 per cent respectively.

SUMMARY

Observations of the behavior of arsenical and nonarsenical phosphorized copper in the production of seamless tubing indicates that as much as 0.2 per cent arsenic has no measurable effect on the behavior of the tubing during fabrication. Both arsenical and nonarsenical copper can be given drastic reductions in area without intermediate annealing, and the same power is required for drawing arsenical copper as for arsenic-free copper, as shown by these tests.

Tensile tests prove that arsenic increases the strength of the cold-drawn tubing somewhat, but has no measurable effect on the strength of annealed tubing. The ductility of the tubing, as evidenced by the elongations found in the tensile tests and other tests described above, is unaffected by 0.20 per cent arsenic.

On the basis of the present tests it is concluded, therefore, that in the range of reductions dealt with, arsenic has no appreciable effect on the fabricating characteristics of copper.

Directional Properties in Cold-rolled and Annealed Commercial Bronze

By Arthur Phillips,* New Haven, Conn. and Carl H. Samans,† Waterbury, Conn.

(Buffalo Meeting, October, 1932)

The study of anisotropy in metals has been greatly stimulated in recent years by the rapid development of X-ray methods for determining the crystallographic relationships of wrought and annealed materials. Prior to this time the knowledge regarding the directional properties of commercial alloys consisted almost exclusively of observations of a practical nature made during the fabrication of metal objects, supplemented by a limited number of mechanical tests on specimens cut at various angles to the direction of working. Such observations clearly indicate that the common methods of cold-working metals cause both a crystallographic and a mechanical fibering varying in character and degree according to the nature and extent of the deforming process. Even after annealing, following certain not too well known combinations of reductions and anneals, a preferred orientation may exist, thereby constituting a residual fiber effect sufficiently pronounced to manifest directional properties.

With the application of the X-ray the experimental horizon was extended chiefly because the study of anisotropic metals promised to offer direct and quantitative evidence regarding the involved mechanism of fragmentation and plastic flow. As a natural consequence the intensive studies in this direction have yielded a vast accumulation of data of ultimate potential value. Unfortunately, however, as is commonly the case in entering a virgin field of experimentation, many of the data cannot be molded into complete and coherent form because of the many unrelated conditions of the experimental projects. Again, the results of the study of single crystals have been rather naturally but at times indiscriminately applied to polycrystalline metals. Furthermore, sweeping statements have been made regarding the behavior during working and annealing of metals and alloys, entirely on the basis of similarity in lattice arrangement. There is abundant reason for believing that relatively small concentration variables, differences in magnitude and distribution of applied stresses, and the character of associated annealing treatments may in some cases greatly influence the mechanics of flow and consequently largely determine the final structural characteristics of the metal.

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* Associate Professor of Metallurgy, Yale University.

† Chase Brass & Copper Co.

The rather extreme anisotropic conditions frequently found in annealed materials lead to local but usually symmetrical plastic flowing under applied stresses. This tendency is commonly manifested in varying degrees by the formation of "ears" or "tips" on drawn objects. The differential yielding of the metal is extremely troublesome in that its cause is often difficult to determine and, for this reason, the remedy is necessarily sought by "cut and try" methods.

Recently one of the writers published the results of a series of tests detailing some of the directional tendencies of two kinds of copper in the cold-rolled and annealed states.[1] The present paper deals with a broader study of fiber effects, in that it includes not only the tensile properties but also cupping tests, which are generally considered to be extremely sensitive in revealing anisotropy in annealed metals. A study of the fiber texture of the variously treated specimens will be published at a later date.

Although some attention has been paid to the directional differences in tensile properties and other mechanical properties of wrought metals, and at least one investigator[2] has measured the height of ears on copper cups drawn from metal subjected to a wide range of treatments, as far as we are aware no systematic study has been published which attempts to correlate cupping and tensile results on specimens that have received rolling and annealing treatments sufficiently diverse to cover the latitude of common mill practices. It is frequently stated by mill operators that the ordinary tensile test is no criterion as to whether or not a material will produce ears on cupping. This question should be answered by the results of this experimental program.

Preparation and Composition of Material

The composition of the brass used in this work was as follows: copper, 90.08 per cent; zinc, 9.88; lead, 0.012; iron, 0.030. This alloy, commonly known as commercial bronze, was selected because of its wide application where deep-drawing properties are essential. It may be added, also, that this brass is rather prone to develop ears under certain combinations of mill treatments.

Five bars of this analysis were cast from the same round. Each bar was tested for specific gravity and fracture, in order to establish the soundness of the metal. It was decided to restrict the rolling and annealing treatments to limits fairly representative of current mill practice in order to obtain data of practical significance. Each bar was rolled on a separate schedule to a thickness of 0.032 in. The treatments chosen were as follows:

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[1] A. Phillips and E. S. Bunn: Directional Properties in Cold-rolled and Annealed Copper. *Trans.* A.I.M.E. (1931) **93**, Inst. Metals Div., 353.

[2] K. Kaiser: Die Entstehung von unebenen Rändern und Hohlkörpen aus Kupferblech. *Ztsch. f. Metallkunde* (1927) **19**, 435.

Bar A. Light reductions with light anneals.
Bar B. Light reductions with high-temperature anneals.
Bar C. Moderate reductions with light anneals.
Bar D. Moderate reductions with high-temperature anneals.
Bar E. Very heavy reduction.

The schedules are given in greater detail in Table 1.

TABLE 1.—*Rolling and Annealing Schedules*

A	B	C	D	E
Rolled to 0.625 in. Annealed, 600° C. Overhauled Rolled to 0.325 in. Annealed, 600° C. Rolled to 0.204 in. Annealed, 600° C. Rolled to 0.128 in. Annealed, 600° C. Rolled to 0.081 in. Annealed, 600° C. Rolled to 0.051 in. Annealed, 600° C. Rolled to 0.032 in. Final reduction = 37 per cent	Rolled to 0.625 in. Annealed, 800° C. Overhauled Rolled to 0.325 in. Annealed, 800° C. Rolled to 0.204 in. Annealed, 800° C. Rolled to 0.128 in. Annealed, 800° C. Rolled to 0.081 in. Annealed, 800° C. Rolled to 0.051 in. Annealed, 800° C. Rolled to 0.032 in. Final reduction = 37 pre cent	Rolled to 0.625 in. Annealed, 600° C. Overhauled Rolled to 0.181 in. Annealed, 600° C. Rolled to 0.072 in. Annealed 600° C. Rolled to 0.032 in. Final reduction = 56 per cent	Rolled to 0.625 in. Annealed, 800° C. Overhauled Rolled to 0.181 in. Annealed, 800° C. Rolled to 0.072 in. Annealed, 800° C. Rolled to 0.032 in. Final reduction = 56 per cent	Rolled to 0.625 in. Annealed, 700° C. Overhauled Rolled to 0.032 in. Final reduction = 95 per cent

TESTS ON THE HARD-ROLLED MATERIAL

It was decided to make tensile tests in five directions on the hard-rolled sheets. Three test pieces were prepared, cut at the following angles with respect to the rolling directions: 0°, 22.5°, 45°, 67.5° and 90°. The testing data so obtained, including Rockwell hardness tests, are summarized in Table 2, and graphically shown in Fig. 1. In general, it may be stated that the transverse (90°) strength is the highest; furthermore, the strength values increase progressively from the 0° to the 90° positions, with the possible exception of the 22.5° direction, which seems to show a slight minimum point in the material with light and moderate reductions. In the severely rolled brass (E) the curve rises steadily from the longitudinal (0°) value until an increase in strength of approximately 17 per cent is attained in the transverse test. It is interesting to note the difference in strength values of the C and D series, which clearly indicates that, although the lower temperature of anneal prior to the last reduction

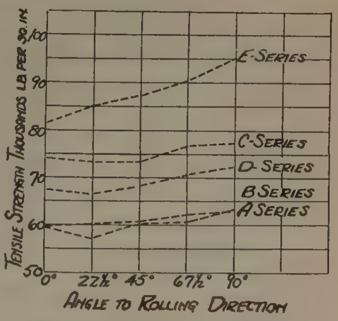

FIG. 1.—DIRECTIONAL STRENGTH PROPERTIES OF COLD-ROLLED 90–10 BRASS.

TABLE 2.—*Properties of Rolled Material*

Series	Rockwell B, 1/16-in. Ball, 60-kg. Load	Tensile Strength, Lb. per Sq. In.					Elongation in 2 In., Per Cent				
		0°	22.5°	45°	67.5°	90°	0°	22.5°	45°	67.5°	90°
A	98.5	59,300	57,200	60,400	60,900	63,450	2.7	3.0	2.75	3.0	3.2
B	98.0	59,950	60,050	60,600	62,200	63,050	2.8	3.0	3.0	2.7	2.5
C	104.0	74,000	73,100	73,500	76,800	77,300	4.0	3.5	3.0	3.0	3.0
D	101.5	67,600	66,500	68,200	70,800	72,500	3.0	3.0	2.5	2.0	2.5
E	107.5	81,800	85,100	87,000	90,400	95,200	5.0	4.0	4.0	3.5	3.5

gives the higher strength, the relative directional properties are essentially the same.

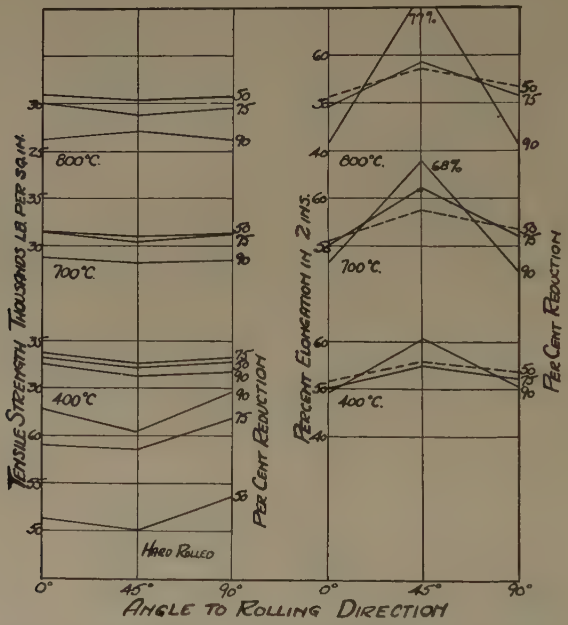

FIG. 2.—DIRECTIONAL PROPERTIES OF COLD-ROLLED AND ANNEALED TOUGH-PITCH LAKE COPPER.

It might be appropriate to emphasize what seems to be an important difference between copper and brass in the work-hardened condition. According to Phillips and Bunn,[3] the transverse strength of copper of normal oxygen content reduced 90 per cent is only about 3 per cent greater than the strength longitudinally. Furthermore, there is a decided minimum point in the 45° direction. For comparison with the 90–10 brass, typical results of similar tests on copper have been included in Fig. 2.

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[3] Reference of footnote 1.

Bauer, Göler and Sachs[4] have made the same observation with respect to the minimum point at 45° and state that a brass containing about 98.5 per cent copper represents in this respect a transition alloy between copper and the higher zinc-content alpha brasses.

TESTS ON THE ANNEALED MATERIALS

From each of the rolled strips 15 specimens were cut in each of the five directions previously mentioned. Three of each series were annealed for 30 min. at 400°, 500°, 600°, 700° and 800° C. This program necessitated the heat-treating and tensile-testing of 375 strips. From each rolled sheet 30 pieces were removed for the cupping tests. Six samples from each of the five materials were annealed at the temperatures mentioned above. In other words, measurements were made on 150 cups. After the square pieces were annealed they were cut and drawn in one operation, using a blank diameter of 2.058 in. and a die diameter of 1.120 in. The reduction of the cup wall was approximately 45.5 per cent. The cups were drawn with the rolling direction of the original sheets in the same direction with respect to the press set up. Table 3 details the

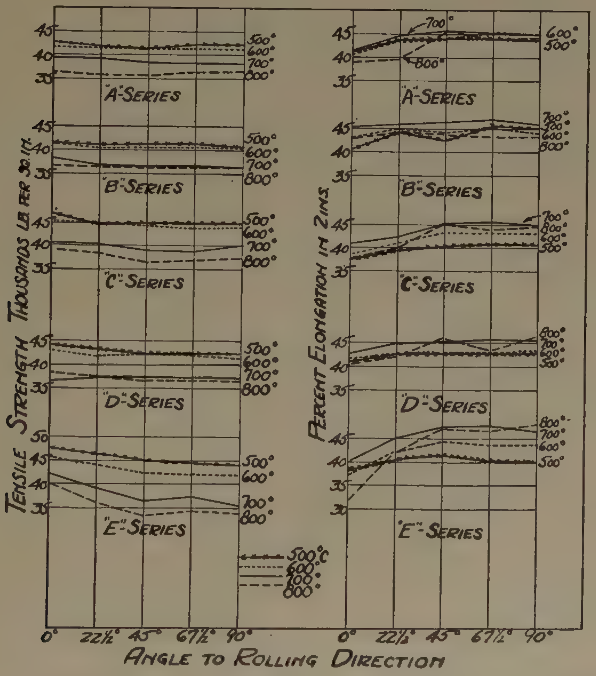

FIG. 3.—DIRECTIONAL PROPERTIES OF ANNEALED 90–10 BRASS.

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[4] O. Bauer, F. Göler und G. Sachs: Untersuchungen an Kupfer und Messing. *Ztsch. f. Metallkunde* (1928) **20**, 202.

average values of the Rockwell hardness, grain size, tensile and cupping tests. The tensile and elongation values are shown in Fig. 3.

TABLE 3.—*Properties of Annealed* 90–10 *Brass*

Series	Temperature of Anneal, Deg. C.	Grain Size, Mm.	Rockwell B, 1/16-in. Ball, 60-kg. Load[a]	Tensile Strength, Lb. per Sq. In.[b]					Elongation in 2 In., Per Cent[b]					Height Ears, In.[c]
				0°	22.5°	45°	67.5°	90°	0°	22.5°	45°	67.5°	90°	
A	400		90.5	51,600	52,300	49,000	47,300	48,000	16.5	13.0	16	25.5	26.5	*d*
	500	0.011	66.5	42,600	41,700	41,550	42,150	42,250	41.3	43.5	43.7	44	44	<0.005
	600	0.012	64	41,450	41,100	41,150	41,150	41,250	40.6	43	43.5	45	44.6	<0.005
	700	0.018	57.5	39,360	39,200	38,580	38,200	38,300	41.5	44	45.3	45.0	45.3	<0.005
	800	0.070	53	36,350	35,850	35,800	36,350	36,750	39	39.6	45	44	44	0.011
B	400		89	49,700	48,100	47,700	47,000	47,900	18	17	17.0	20.5	23.5	*d*
	500	0.014	64	41,650	41,000	41,170	41,130	40,950	40.5	44	42.6	45.5	45.3	∠0.003
	600	0.017	63.5	41,050	40,100	40,550	40,500	40,400	43	45	44	45	44	∠0.005
	700	0.032	56	37,200	36,900	36,400	36,700	36,500	45.5	46	46.5	47	46	absent
	800	0.045	53.5	36,900	36,150	36,200	36,650	36,250	42.8	44	44	43.3	43.1	absent
C	400		77.5	46,700	45,600	44,800	45,200	45,200	39	39	41	40.5	41	*d*
	500	<0.009	75.5	47,000	44,100	44,700	44,850	44,800	37.3	39.1	41.2	41.7	41.7	0.009
	600	<0.009	71.5	45,300	44,700	44,300	43,800	43,800	38.5	41	43	43	43	0.008
	700	0.010	64	40,700	40,200	39,100	39,000	40,200	41	42.5	45	45.5	45	0.011
	800	0.037	59	39,150	38,150	36,300	37,000	37,750	37.5	39.5	45	44	44.5	0.035
D	400		78.5	45,900	45,500	44,300	49,800	48,500	32.5	32.5	38.5	23	34	
	500	0.010	69.5	44,100	43,300	42,400	42,700	42,200	41	43	43	43	43	<0.005
	600	0.014	66.5	43,100	41,800	42,200	42,100	41,300	42	43	43	43	44	<0.005
	700	0.030	60	36,700	37,800	37,400	37,600	37,500	43	45	45.5	46	46	<0.005
	800	0.039	59.5	38,300	37,300	36,800	36,750	36,500	40.6	42.3	46	43.5	46.5	0.008
E	400		82.5	48,400	47,600	46,300	49,500	45,300	37	39	37.5	34	38	
	500	<0.009	77	48,000	46,350	45,000	44,300	44,400	38	40.5	41.2	40.2	40.2	0.011
	600	0.012	65.5	45,900	44,350	42,500	42,150	42,150	37.5	42	44.5	43.7	44	0.014
	700	0.027	55	42,200	39,100	36,700	37,500	35,800	40	45	47.5	47.5	46.5	0.023
	800	0.052	50.5	40,300	36,200	33,600	34,500	34,100	32	42	47	46.5	48	0.054

[a] Average of ten tests.
[b] Average of three tests.
[c] Average of six tests.
[d] Not completely recrystallized.

Considering first the tensile strength, it is evident that the A and B series, representing low-temperature and high-temperature anneals respectively, give almost identical absolute values and show no pronounced directional differences. The C and D series (moderate prior reductions with low-temperature and high-temperature anneals, respectively) give somewhat higher tensile values than the A and B series, especially for the final anneals at the lower temperatures. This difference, of course, indicates the significance of the heavier reductions prior to the last anneal. Also C, in which the intermediate anneals were at the lower temperatures, yields higher strength values than D, in which the anneals were at higher temperatures but following same reductions. Furthermore, the C series begins to display some directional differences, particularly after the higher final anneals. In the E tests, final reduction 95 per cent, there are decided differences, again more evident after the anneals at the higher temperatures. The tensile strength drops from a maximum value in the longitudinal direction to the 45° value which holds almost constant through the 90° position, although there does appear to be a slight increase at 67.5°. For example, after an anneal at 800° C. the longitudinal specimens were about 18 per cent stronger than the transverse pieces.

Considering next the elongation values, we find significant differences in spite of unavoidable irregularities due to the nature of the test. Reviewing series A, B, C and D collectively, it appears that in general the trend is upward from the 0° to the 45° position and that then the value is maintained to the 90° direction. This again is especially true of the higher anneals. In the E series there is a striking difference in elongation values from 0° to 90°. For the 800° C. anneal the elongation increases from 32 to 48 per cent—an increase of 50 per cent.

From the results of the cupping tests as shown in Table 3 it is obvious that the height of the ears parallels the directional differences found by the tensile tests. In all cases, the four ears were found at 45° to the rolling direction. After certain treatments the ears formed were too small to be measured accurately and these results were tabulated as <0.005 in. It was found possible, however, to make a more definite comparison of these groups by visual examination. For example, it can be said that the A group showed a greater tendency to ear than the B; likewise, the C developed higher ears than the D. In other words, for the same intermediate and final reductions and the same final anneal, the lower the intermediate anneals the greater was the tendency to ear. As might be expected from the tensile data, the highest ears were found in the E series. In the cups of this series annealed at 800° C. an average ear height of 0.054 in. was attained.

A casual inspection of the cups of each series showed that the troughs bisected by the rolling direction of the sheet were lower than the other pair. For example, a typical set of measurements around the cup (made on the E series; 800° C. anneal) is given in Table 4.

TABLE 4.—*Typical Measurements around a Cup*
INCHES

High	Low	Difference	Mean	Position of Low Point on Cup
0.684	0.639	0.045		90° to rolling direction
0.681	0.616	0.065	0.048	0° to rolling direction
0.672	0.622	0.050	0.062	90° to rolling direction
0.678	0.620	0.058		0° to rolling direction
Average.....			0.055	

It is significant that the low troughs bisected by the rolling direction lie in the direction of minimum elongation; namely, the longitudinal direction of the strip.

COMPARISON OF 90–10 BRASS WITH COPPER

Attention has already been drawn to what seems to be a fundamental dissimilarity in the character of the directional properties of copper and brass after reductions by cold working. Bauer, Göler and Sachs[5] have stated that this difference is not suggested by X-ray diffraction patterns of worked brass and copper. No differences in orientational characteristics were observed by them. We are inclined to believe that a more complete analysis of the fiber texture by the pole figure method as described by Wever[6] would reveal significant differences.

As a basis for comparison of the properties of the materials in the annealed state we are showing (Fig. 2) the results of a series of tests, previously made and described on tough-pitch Lake copper. Copper seems to show a minimum point in tensile strength at 45° with the exception of the metal very severely worked and annealed at very high temperatures. After a 90 per cent reduction and a 700° C. anneal this minimum practically disappears and after an 800° C. anneal the 45° direction reaches a slight maximum. A still more pronounced difference between copper and brass is shown by a study of the elongation results. In copper the 45° position shows a decided maximum over the approximately equal longitudinal and transverse values. This maximum becomes higher with increasing reductions and higher annealing temperatures. In the copper annealed at 800° C. following a 90 per cent reduction the elongation at 45° was 77 per cent as compared with approximately 40 per cent for the 0° and 90° positions. As mentioned before, in brass the elongation increased from the longitudinal direction to the 45° position and then remained practically constant up to and including the transverse position.

We are inclined to believe that these distinctions in properties are further manifested by a difference in cupping characteristics. In spite of the serious troubles caused by the formation of ears on drawn articles little information of a positive nature regarding the location of the ears on the various metals can be found in the literature. It seems to be assumed by many mill operators that, in both copper and brass, they may appear at 45° to the direction of rolling, or in and at right angles to this direction. As far as we have observed, and our experience is admittedly limited, the ears on brass appear without exception at the 45° directions. Likewise, without exception, they are found in and at right angles to the rolling direction in drawn copper articles. Our observations with regard to copper are consistent with the results of our directional tests. Furthermore, they are in harmony with the X-ray studies of severely rolled and annealed copper. It is generally believed that copper so treated is oriented with a cube face in the rolling surface and a cube edge parallel to the rolling direction. If this is a correct statement of the orientation characteristics, it seems evident that copper with a decided preferred orientation develops ears at the 0° and 90° positions through slip on the octahedral planes. Most certainly in this metal the ears do not as a rule appear in the direction of maximum elongation; that is, the 45° direction.

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[5] Reference of footnote 4.

[6] F. Wever: Texture of Metals after Cold Deformation. Trans. A.I.M.E. (1931) **93,** Inst. Metals Div., 51.

The writers believe, however, that specific statements regarding the directional tendencies in copper should be made cautiously. There is good reason for believing that relatively small amounts of alloying elements, such as the residual material present after deoxidation, exert a considerable influence on the directional properties of this metal. For example, copper deoxidized by phosphorus and containing a slight excess of this element did not exhibit the same type of fiber as the tough-pitch lake copper referred to in this paper, although the rolling and annealing treatments were identical.

According to Kaiser[7] the location of the ears on copper cups is largely dependent on the next to the last anneal. He says that if this anneal is below about 650° C. the ears will appear in and at 90° to the rolling direction; for higher temperatures, at the 45° positions. Although the writers have made no cupping tests on copper to check Kaiser's conclusions, they have studied the directional properties of electrolytic and tough-pitch Lake, which have had "get ready" anneals at 350° and 850° C. For all temperatures of final anneal the tensile directional properties of the sheets were unquestionably of the same nature irrespective of the temperature of the next to the last anneal. For this reason we would expect the ears to form at the same locations.

We do not wish to take the attitude, however, that copper cups cannot be produced with 45° ears. It is conceivable that ears so located can be formed from copper containing small amounts of certain alloying elements, or even by specific combinations of rolling and annealing treatments. We are reliably informed that cupronickel under distinctly different treatments shows both types of ears.

SUMMARY

1. The most pronounced tensile directional properties and the greatest earing tendency are obtained in a 90–10 brass given the greatest reductions followed by high temperatures of anneal.

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[7] Reference of footnote 2.

2. The ordinary tensile test applied to strip brass cut at several angles to the rolling direction seems to be of significance in indicating whether or not annealed brass will form ears on drawing.

3. In slightly and moderately worked brass, the lower the temperature of the intermediate and next to the last anneals, the more marked are the directional differences as shown by both tensile and cupping tests.

4. Copper seems prone to form ears in and at right angles to the rolling direction. The 90–10 brass, as well as other brasses observed by the writers, drew with ears at 45° to the direction of rolling.

5. The directional properties of copper are quite different in character from those found in the 90–10 brass.

Acknowledgments

The writers wish to express their indebtedness to Dr. D. K. Crampton, of the Chase Brass & Copper Co., for his interest and assistance in this work. They also wish to thank the Chase Brass & Copper Co. for supplying and preparing the material used in the experimental program.

[For discussion, see page 187.]

Ears on Cupronickel Cups

BY W. H. BASSETT[*] AND J. C. BRADLEY,[†] WATERBURY, CONN.

(Buffalo Meeting, October, 1932)

IN their paper on the directional properties in cold-rolled and annealed commercial bronze,[1] Phillips and Samans suggest that cupronickel, under distinctly different treatments, shows both "45° ears" and "90° ears." Fig. 1 shows the ears on some cupronickel cups made some 17 years ago for bullet jackets for small arms ammunition. In this case the material heated to 425° C. had "45° ears," while that annealed at 950° C. showed long "90° ears" when drawn with the same tools. The method of cupping, the shape of cupping tools, etc., were found to have very little influence on the earing tendency, but the deeper the cup was drawn, the higher the ears would be.

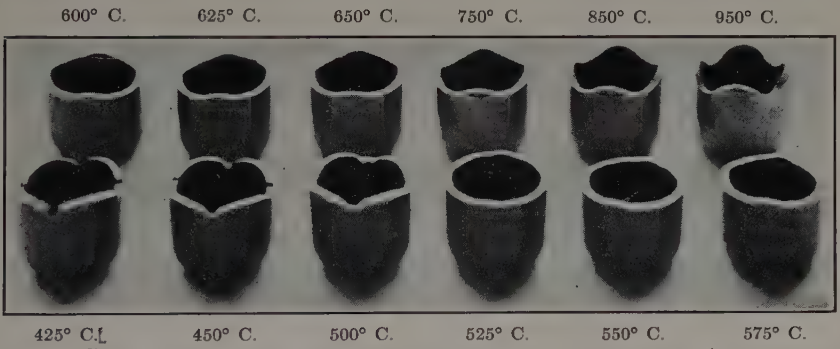

FIG. 1.—CUPRONICKEL, 0.032-in. GAGE, CAST WITH MAGNESIUM. ANNEALED AT TEMPERATURES INDICATED (DEGREES CENTIGRADE) AND CUPPED.

METHOD OF MANUFACTURE

Cupronickel cast bars were 1 in. thick. Ordinarily, they were rolled with numerous passes to a thickness of 0.4 to 0.2 in., according to conditions. They were then given a single intermediate anneal, and rolled to finish thickness, frequently 0.032 in. After a last anneal the material was cupped with a "cut and draw" operation. Progress of this is indicated in Fig. 2, illustrating five different stages at which the drawing was interrupted. The upper line of cups in the figure shows how the 90° ears formed in one lot of metal and the lower line how the 45° ears formed in another lot.

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[*] Metallurgical Manager, The American Brass Co.

[†] Assistant Metallurgist, The American Brass Co.

[1] A. Phillips and C. H. Samans: Directional Properties in Cold-rolled and Annealed Commercial Bronze. See page 171, this volume.

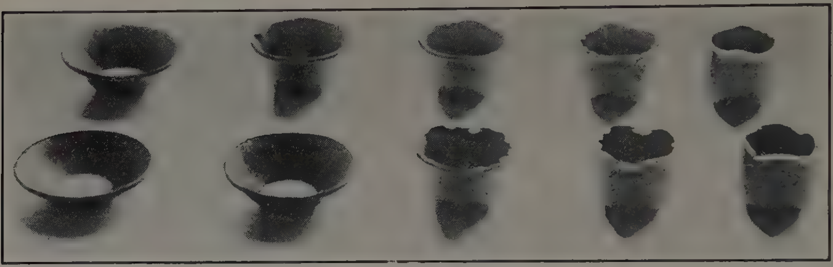

FIG. 2.—CUPRONICKEL, 0.032-IN. GAGE, SHOWING PROGRESS OF EARING TENDENCY DURING CUPPING PROCESS.
Upper row, 90° ears; lower row, 45° ears.

EFFECT ON EARS OF VARYING INTERMEDIATE ANNEALING POINT

Some rolling and annealing experiments were made in which the one intermediate annealing point was varied over the range 0.750 to 0.050 in. or 0.045 in. These showed that for a given casting a certain thickness of metal could be found at which the intermediate anneal could be given so that there would be no ears on the cups. When the intermediate anneal was introduced at a thicker gage, the cups had 90° ears. If the inter-

TABLE 1.—*Height of Ears on Cupronickel Cups, Metal Cast with Manganese*

Gage for Intermediate Anneal, In.	Height of Ears, In.					
	600° C. Final Anneal at 0.032 In.		700° C. Final Anneal at 0.032 In.		800° C. Final Anneal at 0.032 In.	
	90° Ears	45° Ears	90° Ears	45° Ears	90° Ears	45° Ears
1.00		0.022	0.007		0.013	
0.750	0.000	0.000	0.026		0.025	
0.590		0.006	0.020		0.038	
0.460		0.009	0.015		0.030	
0.368		0.012	0.010		0.010	
0.300		0.018		0.002	0.002	
0.240		0.015		0.015		0.012
0.190		0.013		0.017		0.015
0.150		0.021		0.021		0.015
0.090		0.024		0.015		0.016
0.070		0.024		0.016		0.014
0.045		0.019		0.009		0.007
0.032		0.008		0.002	0.000	0.000

mediate anneal was introduced at a thinner gage, the cups had 45° ears. In Table 1, under 700° C., can be seen the effect of changing the intermediate anneal point. When this was at 0.750 in., the cups from a particular bar of metal had 90° ears, 0.026 in. high. With the intermediate anneal at 0.300 in. the ears were almost negligible; that is, 0.002 in. When the intermediate anneal was introduced at a gage less than 0.300 in., 90° ears no longer formed, but 45° ears were the rule, the height of the ears being a maximum when the intermediate anneal was at 0.150 in. The height again became negligible when the metal was rolled directly from 1 in. to the finish 0.032 in. and annealed only at that point. These data are plotted on the middle curve of Fig. 3.

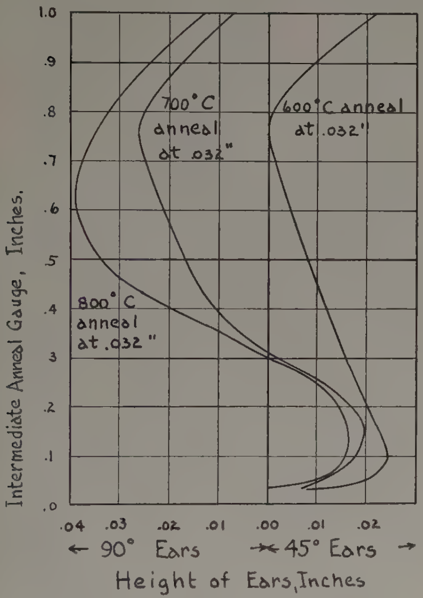

FIG. 3.—EFFECT OF INTERMEDIATE ANNEALING POINT AND TEMPERATURE OF FINAL ANNEAL ON EARING OF CUPRONICKEL CUPS.

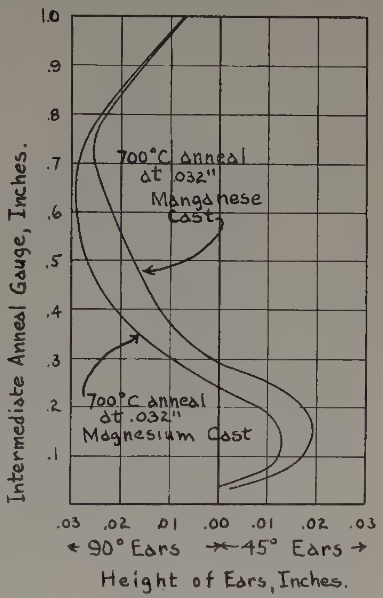

FIG. 4.—EFFECT OF INTERMEDIATE ANNEALING POINT AND COMPOSITION ON EARING OF CUPRONICKEL CUPS.

EFFECT OF FINAL ANNEAL ON EARS

A certain amount of ear control is possible on material given one intermediate anneal if careful attention is paid to the last anneal. The experimental data of Tables 1, 2 and 3 and the plot in Fig. 3 indicate that the higher the final annealing temperature is, the higher the 90° ears will be. This is illustrated in Fig. 1, which also brings out another point—that 45° ears appeared on cups made from material finally heated below the minimum recrystallization temperature (515° C.) and which still showed the structure usual with heavy reductions.

EFFECT OF COMPOSITION ON EARS

Varying the composition of the cupronickel had considerable effect on ears. The experimental data of Table 1 were taken on cupronickel cast with manganese as a deoxidizer. In this case there were practically no ears with an intermediate anneal at 0.300-in. gage and a final

TABLE 2.—*Height of Ears on Cupronickel Cups, Metal Cast with Magnesium*

Gage for Intermediate Anneal, In.	Height of Ears, In.					
	600° C. Final Anneal at 0.032 In.		700° C. Final Anneal at 0.032 In.		800° C. Final Anneal at 0.032 In.	
	90° Ears	45° Ears	90° Ears	45° Ears	90° Ears	45° Ears
1.00	0.002		0.007		0.018	
0.750	0.015		0.027		0.026	
0.590	0.003		0.028		0.034	
0.460	0.005		0.026		0.028	
0.368	0.002		0.014		0.017	
0.300		0.003	0.009		0.011	
0.240		0.013	0.002		0.004	
0.190		0.015		0.011		0.008
0.150		0.015		0.012		0.011
0.090		0.015		0.012		0.009
0.070		0.015		0.010		0.010
0.045		0.024		0.002	0.000	0.000
0.032	0.000	0.000	0.000	0.000	0.000	0.000

TABLE 3.—*Height of Ears on Cupronickel Cups, Metal Cast with New Stock with Magnesium*

Gage for Intermediate Anneal, In.	Height of Ears, In.					
	600° C. Final Anneal at 0.032 In.		700° C. Final Anneal at 0.032 In.		800° C. Final Anneal at 0.032 In.	
	90° Ears	45° Ears	90° Ears	45° Ears	90° Ears	45° Ears
1.00	0.013		0.026		0.025	
0.740	0.009		0.019		0.023	
0.600	0.028		0.035		0.044	
0.455	0.024		0.034		0.037	
0.310	0.012		0.022		0.032	
0.210	0.000	0.000	0.005		0.013	
0.135		0.008		0.007		0.006
0.090		0.005		0.006		0.006
0.050		0.006	0.000	0.000		0.004
0.032	0.006		0.016		0.029	

anneal at 700° C. With magnesium used as a deoxidizer, on the other hand, with a final anneal at 700° C., the ears became negligible when the intermediate anneal was introduced at about 0.240 in., as shown in Table 2. The effect of the intermediate annealing point in relation to the deoxidizer, the final anneal being 700° C., is plotted in Fig. 4. Table 3 shows experimental results on cupronickel cast somewhat differently from that of Table 2. Magnesium was used but no scrap was added. In this instance the data suggest that the "no ear" condition would have been obtained from a 700° C. final anneal by putting the intermediate anneal at 0.170 inches.

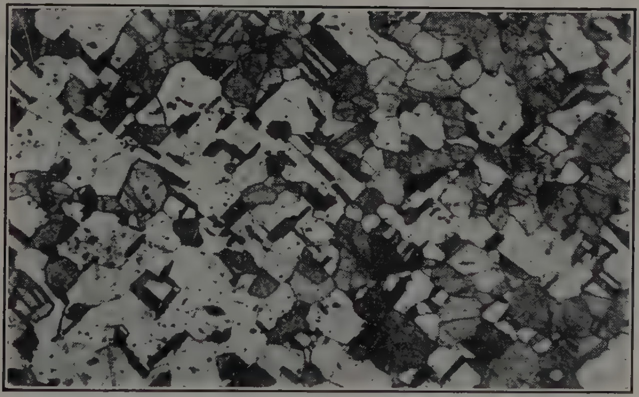

Fig. 5.—Structure of cupronickel often found with 90° ears. × 75.

Frequently when 90° ears were found the microstructure would be regular, "criss-cross" grains, as illustrated by Fig. 5. A number of analyses of such material showed the carbon present in combined form. In one lot of metal, however, carbon was present as graphite, and there were no ears on the material, which had had an intermediate anneal at 0.350 in. The crystals were irregular in shape, the regular grain growth no doubt having been obstructed by the graphite.

The following analysis is typical of the cupronickel cast with manganese: copper, 84.66 per cent; nickel, 14.99; manganese, 0.28; iron, 0.18; zinc, 0.00; lead, 0.007; silicon, 0.015; total carbon, 0.045; graphite, 0.000; nickel oxide, 0.002. When magnesium was used there was no manganese present and the magnesium was about 0.015 per cent. When graphite was present it was in an amount approximating 0.020 per cent.

Effect of Annealing the Casting

Ordinarily the cupronickel castings were not annealed prior to rolling. For experimental purposes a portion of a casting was heated at about

750° C. for three days. The cored structure of cast metal was changed by this treatment to a regular polygonal structure. When the material was rolled to 0.450 in., annealed, rolled to 0.032 in. and portions annealed at 650°, 750°, 850° and 950° C., all samples showed 90° ears. The ears were 0.040 in. high from the material annealed at 850° C. Another portion of the same casting was not annealed but otherwise was treated as before; again 90° ears formed. In this the longest ears were only 0.020 in. high and no ears developed at all after the 850° C. final anneal. Elimination of coring evidently had an effect on directional grain formation and so on earing tendencies.

Still another portion from the casting mentioned above was annealed experimentally at 10 different gages during its reduction to 0.032 in. Then, no matter what the final anneal, there were no ears. The 10 intermediate anneals and the relatively small reductions effectively prevented directional grain growth.

MECHANISM OF EAR FORMATION AND MATERIALS SUBJECT TO EARING

Some years ago F. G. Smith[2] nicely illustrated the effect of directional properties and preferred orientation of crystals by cupping some circles cut from wire gauze (Fig. 6). The 90° ears corresponded with the 45° arrangement of the wires, and the 45° ears with the 90° arrangement.

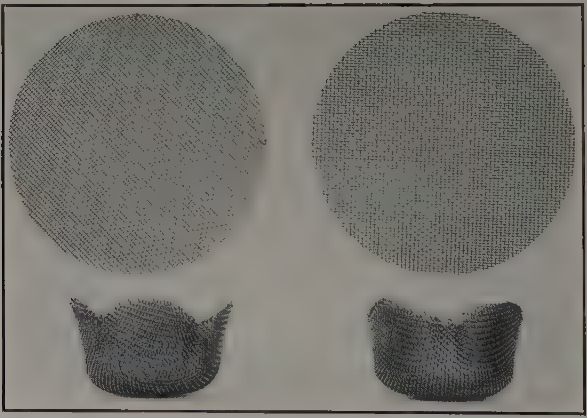

FIG. 6.—EARS ON WIRE-GAUZE CUPS.

In our experience, ears have been found on brass, gilding, copper, aluminum, steel, cupronickel, copper-nickel-zinc alloys and Britannia metal. All steel and copper cups which have been observed have had 90° ears. Cups made from the other materials mentioned excepting cupronickel have had only the 45° ears. However, no detailed study has been made of any other metal like that of cupronickel.

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[2] Sales Engineer, The American Brass Co.

Experience with 80-20 low brass has been with 45° ears. The fourth anneal from the last was 750° C. and the crystals were quite large. The second and third anneals from the last were at 450° C. or lower. On finish annealing at any temperature from 450° to 700° C. the metal made cups with 45° ears. If, on the other hand, the third and second anneals from the last were made at 550° to 650° C., there were no ears.

The 45° ears have been experienced on 65-35 brass. For instance, brass rolled 25 B. & S. numbers hard and finished at 550° C. had very long ears.

Varying the amount of iron, nickel and tin in the brasses was tried, but definite earing tendencies were not found.

Summary

1. The edges of drawn cupronickel cups often have four ears. These may be produced either at 45° to the direction of rolling, or at 90° (and 0°) to the direction of rolling.
2. By systematically reducing the gage of cupronickel at which the intermediate anneal is introduced, a series of cups has been made in which the ears varied in regular fashion as follows: short 90° ears, long 90° ears, shorter 90° ears, no ears, short 45° ears, long 45° ears, short 45° ears, no ears.
3. Variation in composition of the cupronickel affects earing tendencies.
4. The length of the 90° ears increases with the final annealing temperature.
5. Earing evidently is due to directionalism in the arrangement of the crystalline structure and to methods of rolling and annealing which bring about directional arrangement.

DISCUSSION

[This discussion refers also to the paper by Arthur Phillips and Carl H. Samans, which begins on page 171.]

(*E. M. Wise presiding*)

E. M. Wise, Bayonne, N. J.—These papers are of both theoretical and practical importance, for the underlying metallurgical characteristics of the metal influencing the type of orientation produced in the final anneal are not too clear at present, although the increased machining and material costs resulting from badly eared cups are evident. These are matters that are troublesome and even more costly in connection with the precious-metal alloys.

W. B. Price, Waterbury, Conn. (written discussion).—Brass manufacturers who extensively engaged in the manufacture of cupronickel for bullet jackets for small arms ammunition, prior to and during the World War, were familiar with the fact that cupronickel cups formed both 45° ears and 90° ears, and had also devised means for preventing the formation of these ears.

In Fig. 5, Bassett and Bradley show the microstructure of cupronickel often found with 90° ears. The so-called "criss-cross" grains shown are arranged at 45° to each other. This arrangement of the crystals is, of course, identical with the 45° arrangement of the wires (Fig. 6), which produced the 90° ears shown on the wire-gauze cups. Mr. Smith is to be congratulated on the clever way in which he illustrated the effect of directional properties and preferred orientation (Fig. 6) at a time when the metallurgists did not have available X-ray diffraction patterns to differentiate between random and preferred orientation.

Several years ago, I had occasion to observe 90° ears on cartridge gilding (95 per cent Cu, 5 per cent Zn). This particular metal was cast 1¼ in. thick, rolled down to 0.035-in. gage, overhauled at ⅝ in., without an intermediate anneal. This was a reduction of approximately 97 per cent. A photomicrograph of this material showed the same criss-cross grains as Bassett and Bradley show in Fig. 5. The final anneal in this case was between 700° and 800° C. When an intermediate anneal of 550° C. was put in at 0.064-in. gage and a final anneal at the same temperature, the ears disappeared.

A proper coordination of rolling and annealing schedules will eliminate the tendency of nonferrous metals and alloys to form ears.

W. M. Peirce, Palmerton, Pa.—With zinc, which crystallizes in the hexagonal system, it is possible by special rolling to produce experimentally a preferred orientation which results in three sets of ears on cups drawn from the strip.

E. M. Wise.—The relative rates of strain-hardening in the several directions of the sheet during drawing is undoubtedly a factor governing ear formation.

E. H. Dix, Jr., New Kensington, Pa.—In presenting his paper, Mr. Bradley showed a table not included in the preprint, which indicated aluminum as showing ears at 45° to the direction of rolling. While this is generally true, we have found that the addition of as little as 0.2 per cent of an element will change the direction of ears from 45° to 90°.

A. J. Phillips, Perth Amboy, N. J.—This paper makes no mention of gage control and gage difference in the specimens used for cupping tests. It is well known that the ordinary cold-rolled copper alloy strips show a decided crown from center to edge, and in setting up cupping tools it is necessary to allow for this crown. I presume that the authors have tested the material with the direction of rolling at various angles with respect to the cupping tools. This precaution would eliminate variables due to tool set up but would not eliminate the gage factor. For instance, the severely cold-rolled material which after annealing showed the maximum difference in strength value across the direction of rolling would probably also show the maximum amount of "crown." It is just possible that these two factors are somewhat compensating, but it may be that if the crown of the metal were eliminated different results would be obtained.

A. Phillips and C. H. Samans (written discussion).—We are pleased that Messrs. Bassett and Bradley have published the results of their observations on the earing tendencies of cupronickel. Up to date our studies on directional properties have been limited to copper and commercial bronze. Cupronickel has been sadly neglected by previous writers on this subject and for this reason their paper is particularly welcome. Furthermore, cupronickel is somewhat unique in that it seems to draw with 45° or 90° ears depending on the character of the rolling and annealing treatments. Our observations regarding the location of ears in the common metals seem to be in agreement with the statements of the authors, whose experience in this respect is much broader than ours.

The authors remark that in the case of the cups shown in Fig. 1 (p. 183), the 45° ears appear on material annealed below the recrystallization temperature (515° C.). The metal annealed at somewhat higher temperatures showed the 90° type of earing. In other words, they associate the recrystallization temperature range with a transition range between the two types of earing. Such a conclusion might be reached by the evidence of Fig. 1. However, when we turn to the data of the tables this explanation seems less convincing. For example, in Table 1 we find both types of ears in the material annealed at 800° C. If we consider the material which had an intermediate anneal at 0.090 in. we note that after the final reduction of approximately 65 per cent and a final anneal of 800° C. the cups showed pronounced 45° ears; 800° C. is well above the recrystallization temperature for cupronickel reduced 65 per cent.

It is interesting to note that the alloy of Fig. 1 was cast with magnesium. The material of Table 1 was cast with manganese and contained approximately 0.28 per cent manganese and 0.18 per cent iron. The latter alloy showed the greatest tendency to form the 45° ears. With cupronickel made from new stock and cast with magnesium we find fewer examples of the 45° ears, and the 45° ears formed are comparatively low. The authors state that "varying the composition of the cupronickel had considerable effect on ears." This statement cannot be questioned and we are inclined to suggest that the presence of the manganese, magnesium and iron in the relatively small concentrations found in cupronickel may account for the rather unusual earing peculiarities of this alloy. It would be interesting to know whether or not a copper-nickel alloy substantially free of other elements would draw with examples of both the 45° and 90° ears after treatments comparable to ordinary mill practice.

E. M. Wise.—It is possible that very small amounts of a second constituent, graphite for instance, may profoundly affect the mode of recrystallization.

R. L. Templin, New Kensington, Pa.—In studying the directional properties of nonferrous metals, metallurgists might well take advantage of mechanical properties other than tensile strength and elongation. The results of experiments reported by Reid L. Kenyon and Robert S. Burns (Autographic Stress-strain Curves of Deep-drawing Sheets) before the meeting of the American Society for Steel Treating this week might well serve as a guide in similar studies of nonferrous metals. In our own experimental work on aluminum alloys, we have found that the ratio of yield strength to ultimate tensile strength is of considerable significance in considering the drawing qualities and workability of the material.

R. S. Pratt, Bridgeport, Conn. (written discussion).—Some years ago, when we first came in contact with the problem, the mill people were inclined to blame the formation of ears on hard metal. It was also generally believed that high iron content in ordinary sheet brass was associated with the development of ears. A short time ago the opportunity offered to check this point very carefully. A lot of sheet metal that was rejected by the mill because of ununiform anneal was subjected to chemical analyses. The results of the analyses showed that the iron content of the coils in the lot ranged from 0.017 to 0.128 per cent. Cupping tests were made on the coils as annealed by the mill, and failed, with one exception, to show any tendency to form ears in cupping. The lot was then reannealed so as to increase the grain size materially and cupping tests were again made. With the exception of those from three coils, all of the cups showed ears and there was no relation between low iron content and the cups that failed to form ears. The test showed definitely that the iron content in itself was not the cause of ears. They did indicate, however, that in general the larger ears were related to the higher iron content. But the most apparent cause of the formation of ears was the reannealing operation, which increased the grain size.

The marked effect of the reannealing operation led us to check the effect of annealing a material of normal iron content. Numerous cupping tests were made on sheet high brass which had been rolled 4 and 16 hard between the next to the last and final anneals. The next to the last and final anneals were varied so that a number of different conditions were obtained. The cupping tests indicated that ears were formed as readily in the material rolled 4 hard before the final anneal as in material rolled 16 hard, provided the final anneal was made at a temperature sufficiently higher than that used in the next to the last anneal.

In all the work we have done, tensile tests have been made with, across and at 45° to the direction of rolling. These tests indicate the variation in directional properties and the possible tendencies to form ears in cupping. It is still difficult and almost impossible to predict definitely whether or not a given sample or sheet will form ears. It is probable that this is due to the relation of the directional differences in tensile strength to those in elongation.

We have noted, as have the authors of these papers, the differences in the location with respect to the direction of rolling, of ears on copper cups as compared with high-brass cups. It is of interest in this connection to note that such physical tests as have been made to date fail to show the reason why copper forms 90° ears and the brass 45° ears. Such tests as we have made on copper that forms 90° ears showed the same general directional relationship as the tests on brass that gave 45° ears. The work of Phillips and Bunn,[3] published in 1931, confirms this to the extent that maximum elongation and minimum tensile strengths occur at 45° of the grain. Because copper normally forms 90° ears, it would seem more logical if the maximum elongation were in the direction in which the ears are formed. It is unfortunate that physical properties are not available in the paper on cupronickel, for it seems probable that they would help to answer this question.

One of the most significant features of the paper by Phillips and Samans is the presentation of figures that prove the presence of directional properties in annealed sheet much beyond anything realized a few years ago. The possible effect of these differences in other forms of material such as rod or tubing, or another problem in sheet, offers much food for thought.

E. M. Wise.—We must not overlook the fact that finely divided inclusions may dissolve at the temperature finally attained during the anneal and thus not be evident in the sample although they may have been present at lower temperature and have exercised an important influence upon the early stages of the recrystallization. Oxygen in copper may behave in this way.

K. R. Van Horn, Cleveland, Ohio (written discussion).—I compliment the authors on the solution of an earing problem some years before the application of the X-ray to the study of preferred orientation and the focusing of metallurgical attention on the directional properties of metals and the resulting industrial difficulties. Bassett and Bradley's observation that cupronickel may form ears at either 45° or 90° to the direction of rolling, which could be eliminated by a suitable annealing and reduction schedule, is commercially and theoretically pertinent. The result was commercially satisfactory but theoretically is still vague and intriguing. A possible cause of the "versatile" earing tendency of cupronickel has been attributed by the authors to annealing either below or above the recrystallization temperature.

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[3] A. Phillips and E. S. Bunn: Directional Properties in Cold-rolled and Annealed Copper. *Trans.* A.I.M.E. (1931) **93,** Inst. Met. Div., 353.

Also, Professor Phillips suggested a very plausible explanation—that of impurities. I should like to discuss the data submitted thus far and perhaps complicate the situation by the introduction of another factor.

Directional properties generally are attributed to either a mechanical or crystallographic fibering of the constituents. Although considerable emphasis has been placed on the latter because of the recent X-ray discoveries, it would still seem that mechanical fibering—*i. e.*, elongation of metallic and nonmetallic inclusions, physical defects such as pipe, blowholes, etc., in the direction of working—is the probable explanation of the many variations in tensile properties observed in wrought alloys, especially alloys containing an appreciable quantity of impurities. However, in regard to cupronickel, the mechanical fibering explanation would be improbable because of the observed 45° and 90° earing tendency. Consequently, one might turn to the other alternative. The general trend of the curves shown in Fig. 3 (p. 183) suggests crystallographic grain alignment.

R. Glocker,[4] who has exhaustively described preferred orientation in both worked and recrystallized metals, has distinguished three different types:

1. Worked metals recrystallizing with a random orientation.
2. Worked metals recrystallizing and immediately or at a later time forming a recrystallized preference, different from that derived from rolling, which can be removed by heating at higher temperatures.
3. Recrystallized worked metals that form a preferred orientation, either similar or different from the worked, which cannot be obliterated by heating at higher temperatures.

Fig. 3 shows that the higher the temperature of the final anneal, the larger the 90° ears, and that the 90° ears are not formed after a 600° C. final anneal. This might be attributed to a recrystallized preferred orientation forming at or below 700° C. (recrystallization would occur, of course, at a lower temperature defined by the degree of reduction, which might not necessarily be accompanied by the development of a recrystallized preferred orientation), which becomes more pronounced on heating at higher temperatures; *i. e.*, 800° C. The favorable conditions for 90° ears are, therefore, high temperature and low reductions (up to 65 per cent). Cupronickel reduced more than 65 per cent might retain the worked type of grain alignment after recrystallization by heating at 700° and 800° C. and thereby form ears at 45°. It could, also, be postulated that metal annealed at 600° C. did not form 90° ears because a sufficiently high temperature was not attained to remove the effects of the worked preference and, therefore, formed only 45° ears.

The further results of the authors' investigation that magnesium—pure or scrap—affect the height of the ears and the point in the reduction schedule where an intermediate anneal can be inserted to eliminate earing can also be explained by the effect of impurities on the type and time of formation of the preferred recrystallized orientation. The authors also found that cupronickel sheet annealed at ten different gages during the reduction never produced earing. This procedure, involving light reductions and probably complete removal of preference by frequent anneals certainly suggests crystallographic grain alignment in the previous experiments. The above crystallographic explanation of the earing results deserves some consideration inasmuch as copper is known to form a certain type or types of preference on cold rolling and an entirely different type after recrystallization, which becomes more pronounced with increasing annealing temperature. I merely offer this possibility to open another avenue of consideration of this complex problem, although realizing that the evidence is circumstantial and meager.

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[4] R. Glocker: Material Prüfung mit Röntgenstrahlen. Julius Springer, 1927.

I agree with Professor Phillips that the effect of impurities on the earing is great. The substitution of scrap or pure magnesium greatly reduces the 45° earing as compared to manganese-bearing cupronickel. Mr. Dix mentioned that the addition of as much as 0.2 per cent of another element alters the type of earing of aluminum from the general 45° to the unusual 90° ears. Copper ears at 90°, while the copper-tin and copper-zinc alloys ear at 45°. Bauer, Göler, and Sachs[5] have revealed that brass containing 98.5 per cent copper represents the transition alloy, in this respect, between copper and the high-zinc alpha brasses.

It would appear, therefore, that impurities have an appreciable effect on the type of earing and the directional properties; also that a crystallographic alignment might be more effective in cupronickel than mechanical fibering. It would be interesting to know how the impurities consummate this result. Do the impurities alter the type of crystallographic fibering which would inherently give directional properties? Is the influence of impurities more profound than affecting the grain orientation? Do they distort the cohesive relations of the atoms? These questions can only be answered by an examination of the tensile properties (tensile strength, elongation and ratio of yield point to tensile strength as suggested by Mr. Templin), diffraction analysis and an exhaustive investigation of the effect of impurities.

W. H. BASSETT AND J. C. BRADLEY (written discussion).—Messrs. Phillips and Samans and Dr. Van Horn commented on the statement that "45° ears appear on cups made from material finally heated below the minimum recrystallization temperature (515° C.) and which still showed the structure usual with heavy reductions." We had not thought of this heating as having any appreciable influence on the 45° ear formation; for heating below the "recrystallization temperature" would cause no considerable structural change. We suspect the effect of heavy reductions would be more responsible for the 45° ears in this case, for the particular cups shown in Fig. 1 with 45° ears were made from metal still hard after a reduction of approximately 85 per cent.

Dr. Van Horn concludes from Fig. 3 that "favorable conditions for 90° ears are high temperature and low reductions." We believe the statement would be more nearly correct if written "heavy reductions and high temperatures."

We were much interested in Mr. Dix's finding that the addition of as little as 0.2 per cent of an element will change the direction of ears in aluminum from 45° to 90°. This effect is analogous to the change from 90° ears in copper to 45° ears by adding sufficient zinc though the required amount of added element in this case is apparently nearer 10 to 15 per cent. It also seems comparable to the effect of impurities or added elements in cupronickel where these additions change the height of ears.

It seems to be agreed that earing is due to directionalism in the arrangement of the crystalline structure. This is indicated by the physical tests given in the paper by Phillips and Samans; the statement of Mr. Peirce that zinc with its hexagonal system results in three sets of ears; the note by Mr. Price confirming with cartridge gilding our findings about criss-cross grain structure with cupronickel; the influence of added elements brought out by Mr. Dix; the effect of inclusions, etc., emphasized by Dr. Van Horn; and our findings as to the importance of annealing and rolling control.

A. PHILLIPS AND C. H. SAMANS (written discussion).—The nature of the discussions on the two papers on earing characteristics emphasizes the complexity of the conditions associated with the study of directional properties. It is, of course, evident that much remains to be done before any precise evaluation of the many factors influencing fiber formation can be obtained. As the writers have previously stated, it seems necessary to acquire a statistical background based on the testing of many metals that have been given a variety of treatments, and to correlate the results with the fiber analyses obtained by X-ray studies.

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[5] O. Bauer, F. Göler, and G. Sachs: Untersuchungen an Kupfer und Messing. *Ztsch. f. Metallkunde* (1928) **20**, 202.

We are particularly interested in Mr. Pratt's reference to the influence of iron in brass. We are investigating the effect of certain impurities on the directional properties of commercial bronze. Small amounts of impurities cannot only influence the degree of fibering but can also change the fiber characteristics, as has been shown by Mr. Dix in regard to aluminum. With reference to the significance of inclusions as suggested by Mr. Wise, we feel that in wrought metals relatively large inclusions must necessarily form planes of weakness parallel to the rolling direction and thus preclude the possibility of obtaining the maximum values in strength and elongation properties in the transverse and angular directions. The effect of small inclusions in this respect is not definitely known, but it appears that the small particles of cuprous oxide in electrolytic copper have little effect on the directional properties. We agree with Mr. Templin that yield point and tensile strength data may prove of great value in studying the drawing qualities of metal and we hope to include such data in our experimental program.

Dr. Van Horn has referred to the three types of recrystallization structures as described by Glocker. We are inclined to believe that no simple classification of this kind will properly cover the diversity of fiber effects found in the common metals and alloys. There is good reason for believing that the character, as well as the degree, of fiber is influenced by the previous history of the metal. Most of the work devoted to fiber studies by X-ray methods has been restricted to severely rolled material with little or no regard to the initial or intermediate heat treatments.

We have considered the question raised by Mr. Pratt regarding what appears to be a fundamental difference in the location of ears in copper and brass. A possible explanation for the fact that copper cups show ears in the zero and 90° positions while brass shows them in the 45° positions is suggested by the fact that the two metals have different recrystallization (crystallographically) textures. The commonly accepted recrystallization texture for copper is with a cube plane parallel to a rolling plane and a cube direction parallel to the rolling direction. This arrangement puts a dodecahedral direction in an octahedral plane into the surface of the sheet at an angle of 45° to the rolling direction. As this is the slip plane and slip direction for face-centered cubic metals, slip along these planes would tend to pile up metal at the zero and 90° positions, thereby producing ears. We are working out pole figures representing the recrystallization textures of commercial bronze that shows ears and commercial bronze that does not show ears, in order to see whether a similar explanation is possible here.

In reply to Mr. A. J. Phillips, in usual cupping practice the difference in gage across the blank is taken care of by the hold-down. This, of course, will eliminate the possibility of unsymmetrical ears, the type resulting from gage differences, without affecting in any way the symmetrical ears, which probably are of crystallographic origin.

Some Effects of Internal Stress on Properties of Drawn Brass Tubes*

By D. K. Crampton,† Waterbury, Conn.

(Buffalo Meeting, October, 1932)

The object of this work was to obtain and correlate information on effect of internal stress in variously drawn tubes on several properties. Also, a simple approximate method of comparing types of stress distribution in such variously drawn tubes was sought. There is also included some work on comparison of single and polycrystalline materials and effect of different types of operation and preferred orientation.

Preparation of Material

A series of tubes was drawn to study the effect of the type and degree of final reduction on various physical properties and the approximate distribution of stress intensity across the tube wall. The material used all came from a single heat of 70-30 brass melted in a regular production Ajax-Wyatt induction furnace. The analysis of the metal as cast was: copper, 70.36 per cent; lead, 0.04; iron, 0.02; zinc, balance.

The material was cast in "shells" with 4 in. outside diameter and ¾ in. wall thickness. It was drawn part way down according to the usual standard mill schedule and then by suitable individual schedules to finish by a variety of types and degrees of drawing to the same final cases in every instance; namely, 0.750 in. outside diameter by 0.080 in. wall thickness. The exact final draws, together with the percentage area reductions, diameter reductions and gage reductions are given in Table 1.

In fabricating these tubes, rather unusual precautions were observed to insure the elimination of all variables not under immediate study. All intermediate anneals were carried out at about 1200° F. down to the so-called "cut-in size"; namely, 1⁷⁄₁₆ by ³⁄₁₆ in. From this point on, all anneals were made at from 1050° to 1100° F. The greatest care was used all through to have the tubes as free from minor surface defects as possible. When such defects were visible on intermediate sizes they were carefully filed out.

On the final draw to ¾-in. diameter the die was aligned with the greatest possible precision in order to insure as straight a tube as possible as removed from the draw bench. This was considered very important, as any subsequent straightening operation by rolls, bending, Medart machines, etc., would introduce serious changes in intensity and distribution of stress. This had been amply proved by earlier unpublished work. In none of the papers published on this general subject has this been mentioned by any of the authors and it is believed that owing to this possibly some of the reported results may be somewhat in error.

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* From a dissertation presented to the Faculty of the graduate school of Yale University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

† Metallurgist, Chase Brass & Copper Co.

TABLE 1.—*Final Drawing Operations*

Finish Size, 0.750-in. Diameter by 0.080-in. Gage in All Operations

Tube No.	Reduced from		Drawn or Sunk	Area Reduction, Per Cent	Outside Diameter Reduction, Per Cent	Gage Reduction, Per Cent
	Diameter, In.	Gage, In.				
1	1.063	0.074	Sunk	28	29	+8
2	1.000	0.075	Sunk	22	25	+6
3	0.938	0.076	Sunk	17	20	+5
4	0.875	0.077	Sunk	12	14	+4
5	0.813	0.078	Sunk	5	8	+3
6	1.000	0.082	Drawn	28	25	3
7	0.938	0.088	Drawn	28	20	9
8	0.875	0.096	Drawn	28	14	17
9	0.813	0.106	Drawn	28	7	25
10	0.875	0.137	Drawn	47	14	42

The same die was used for all final draws and sinks. It was a straight side 20° angle die with ⅛ in. straight bearing. This particular design of die had been found from previous investigations to give a comparatively long life and to offer less resistance to drawing than many other shapes commonly used, and it was so easily and accurately reproducible in case of need.

Tubes 1 to 5 inclusive form a series of "sunk" tubes, the degree of sink (diameter reduction) varying from 29.5 down to 7.7 per cent, and net area reductions from 28 down to 5 per cent. Tubes 1 and 6 to 9 inclusive form a series all with the approximately constant area of reduction of 28 per cent but with varying "type" of reduction; *i. e.*, varying percentages of diameter and wall reduction. Tube 10 was given a very heavy area reduction (47 per cent) with the least possible diameter reduction. This was intended to show the greatest immunity from tendency to season-crack and the least harmful intensity and distribution of stress possible.

The tests carried out on these tubes were the following: (1) Tensile tests, (*a*) maximum strength, (*b*) per cent elongation, (*c*) apparent elastic limit, (*d*) modulus of elasticity; (2) Rockwell hardness using $\frac{1}{16}$-in. ball, 100-kg. load, B scale; (3) time required to crack in standard $HgNO_3$ solution; (4) stress distribution by modified Fox method; (5) X-ray studies of crystal orientation.

Portions of each of the 10 tubes were carefully relief-annealed and all tests except stress distribution were run at the same time in comparison with the as-drawn tubes. There was not sufficient material for the complete stress tests on the relief-annealed tubes, although the initial stress released by splitting according to the split-ring method gave a good indication that the relief anneal had been effective. This anneal was carried out at 250° C. for 2 hr., a temperature and time that were found suitable from preliminary annealing tests on these tubes.

PHYSICAL PROPERTIES

Tensile Tests

The tests were carried out in triplicate on the 10 brass tubes as drawn and after relief-annealing, the preparation of which was described above. The tubes were pulled in full cross-section with plugged ends, using a Southwark Emery hydraulic testing machine of 20,000 lb. maximum capacity. The machine was equipped with Templin self-aligning grips so that the loading was axial.

The extensometer used was designed by Prof. H. F. Moore and made by the Southwark company. It was designed to minimize the errors inherent in most simple mechanical instruments and to give a single reading which was an average of movements on two diametrically opposite elements of the specimen. One dial division represented 0.001 in. movement of the stem. There was a 5 to 1 lever arm and a 10-in. gage length was used. This meant that one dial division was equivalent to an extension of 0.00002 in. per inch of gage length. Readings could be made easily to one-fifth division but such accuracy of reading was actually found not warranted as other errors amounted to considerably more. The instrument could, however, be relied upon to an accuracy of approximately one-half dial division, equivalent to 0.00001 in. per inch of gage length.

The results were plotted in a manner suggested by Mr. George Colton of the Department of Engineering Mechanics of Yale University. It consisted of plotting the increment of strain per unit increment of stress against the total strain. The same advantages would accrue if the increment of stress per unit increment of strain were used instead. With the particular testing machine and extensometer used, however, the first method appeared the more logical. In this particular application the increment of strain corresponding to a load increment of 250 lb. was used. Inasmuch as the cross-sectional area of these tubes was exactly $\frac{1}{6}$ sq. in., this corresponded to a unit stress of 1500 lb. per sq. in, A typical result is shown in Fig. 1 for tube 10, both as drawn and as relief-annealed.

A critical discussion of methods of plotting stress-strain diagrams and the interpretation of the terms elastic limit, proportional limit, yield point, etc., are outside the scope of this presentation. The method used, however, is very simple and seems to have all the advantages of the methods described by Templin[1] and Tuckerman.[2] The advantages are that (1) it shows that the modulus of elasticity is not a constant within the elastic range, (2) the effect of internal stress is clearly marked, and (3) the apparent elastic limit or yield point is clearly brought out.

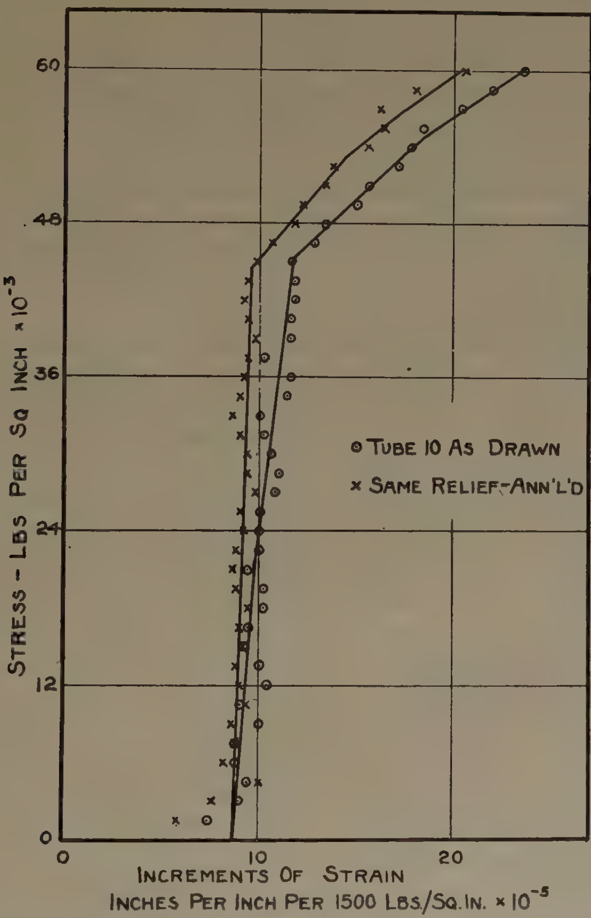

FIG. 1.—STRESS-STRAIN DIAGRAM FOR TUBE 10 AS DRAWN AND RELIEF-ANNEALED.

With the method of plotting shown in Fig. 1, a vertical straight line represents a constant modulus of elasticity. A straight line sloping to the right indicates a uniformly decreasing modulus. The value of the modulus is obtained by dividing the constant increment of stress (in the present work 1500 lb. per sq. in.) by the instantaneous value of the increment of strain. Referring again to Fig. 1, the strain increment at zero load is 0.000088 in. per inch. The modulus at zero load is therefore

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[1] R. L. Templin: The Determination and Significance of the Proportional Limit in the Testing of Metals. *Proc.* Amer. Soc. for Test. Mat. (1929) **29**, II, 523–534.

[2] L. B. Tuckerman: Discussion of reference of footnote 1, 538.

$$\frac{1500}{0.000088} = 17,050,000 \text{ lb. per square inch.}$$

Referring once more to Fig. 1, the curve for the tube in the condition as drawn may be divided into three portions. From 0 to approximately 21,500 lb. per sq. in. stress, the line slopes slightly to the right. From 21,500 to 45,000 lb. per sq. in. it slopes slightly more. Above 45,000 it breaks rather sharply, indicating the apparent elastic limit. The curve for the same tube relief-annealed shows no change of slope whatever corresponding to that in the as-drawn curve at 21,500 lb. per sq. in. Also, up to the apparent elastic limit this curve has appreciably less slope than any portion of the one for the as-drawn tube.

The first break in the as-drawn curve would seem to indicate that internal stresses in the outer fibers were high enough so that the elastic limit of these fibers is reached at the application of an external stress of 21,500 lb. per sq. in. The relief annealing obviously remedies this condition and at the same time greatly reduces the amount of the lowering of the modulus of elasticity with increasing stress. It seems probable that the specimens in question were not perfectly relief-annealed and that, had they been, a constant modulus might have been found below the apparent elastic limit. It is interesting to note that Sayre[3] in his work on mechanical springs has also found a lowering of the modulus of elasticity with applied tensile stress.

The detailed point by point spots for all the tubes in a drawn and relief-annealed condition are omitted for the sake of brevity. In all cases tests were run at least in duplicate, mostly in triplicate. Good agreement was found throughout. For the sake of brevity only the mean figures from the check tests are given. The curves for all tubes are reproduced in Figs. 2, 3 and 4.

Fig. 2 gives for comparison the results for tubes 1 to 5, which form the series with varying degrees of "sink." In the first three there appears a slight break in the curve for the as-drawn tubes in the vicinity of 16,000 to 18,000 lb. per sq. in. This does not appear in the curves for tubes 4 and 5. This is probably because with the lighter working received by these tubes the elastic limit is lower and the magnitude of the stress effect much less. If there were, indeed, a break in these curves as in those for tubes 1, 2 and 3, the sensitivity and accuracy of the extensometer was not sufficient to detect it. All the relief-annealed tubes, however, show a higher and more constant modulus of elasticity than the drawn ones.

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[3] M. F. Sayre: Elastic and Inelastic Behavior in Spring Materials. *Mech. Engineering* (1929) **51**, 915–916.

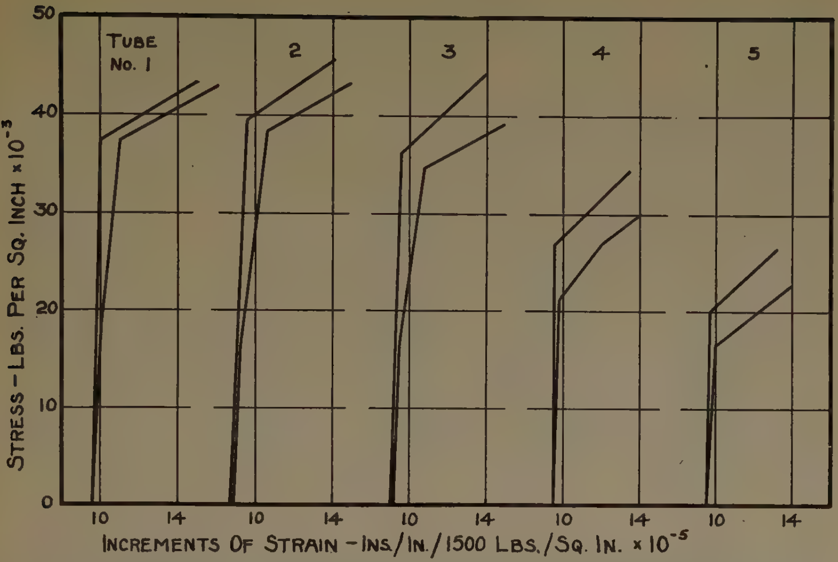

FIG. 2.—STRESS-STRAIN DIAGRAMS FOR TUBES WITH VARYING AMOUNT OF SINK (RIGHT-HAND CURVE OF EACH PAIR AS SUNK; LEFT-HAND AS RELIEF-ANNEALED).

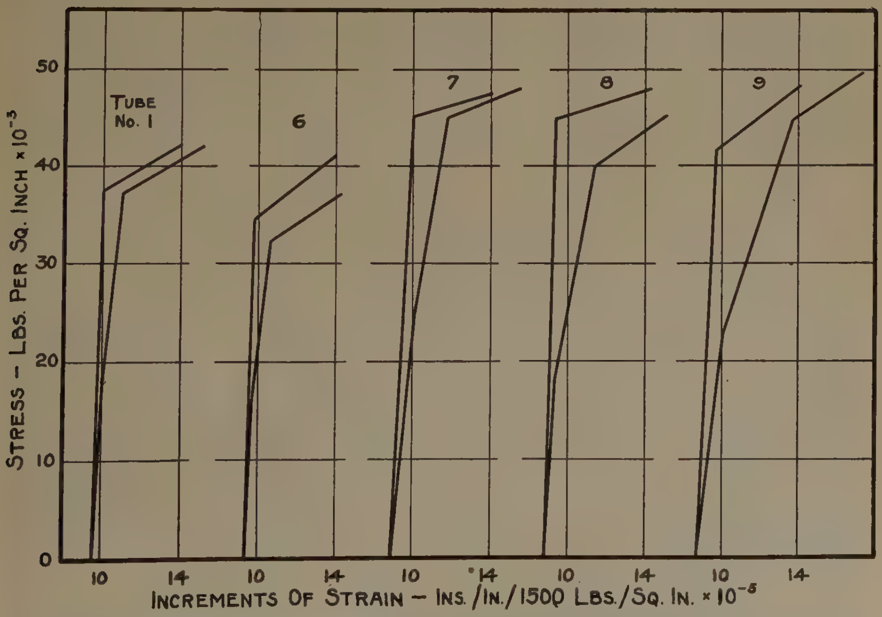

FIG. 3.—STRESS-STRAIN DIAGRAMS FOR TUBES DRAWN 28 PER CENT WITH VARYING DIAMETER AND WALL REDUCTIONS (RIGHT-HAND CURVE OF EACH PAIR AS DRAWN; LEFT-HAND AS RELIEF-ANNEALED).

Fig. 3 gives the same comparison for the series of tubes of constant area reduction but varying diameter and wall reduction. Since all of these tubes had a reduction of the total cross-section area by drawing of approximately 28 per cent, it might have been expected that they would have closely the same strength and apparent elastic limits. Contrary to expectations, however, these tubes show considerable differences in their apparent elastic limits. This increases somewhat as the wall reduction increases and the diameter reduction decreases.

Fig. 4 compares tubes 9 and 10 only. Both of these were drawn with the least possible reduction of inside diameter (barely enough to allow for plug insertion) the difference being that the reduction of cross-section area of No. 9 was 28 per cent and that of No. 10 was 47 per cent. There is not a great difference in the shape of the curves for these two tubes.

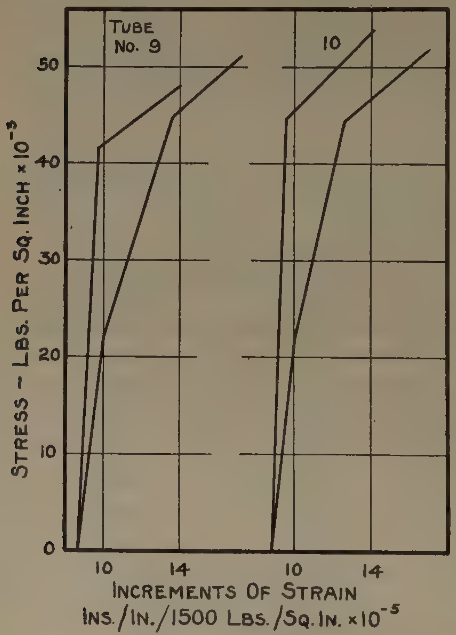

FIG. 4.—STRESS-STRAIN DIAGRAM FOR TUBES WITH LEAST POSSIBLE DIAMETER REDUCTION (RIGHT-HAND CURVE OF EACH PAIR AS DRAWN, LEFT-HAND AS RELIEF-ANNEALED).

Table 2 summarizes the data from the tensile tests and also gives data on the hardness and mercurous nitrate tests which will be described. A study of the tensile strengths in this table shows an insignificant mean difference between drawn and relief-annealed tubes, so that for all practical purposes the effect of relief annealing on the strength may be considered nil. The same is true of the apparent elastic limit, bearing in mind that the accuracy of determination is somewhat less than that of maximum strength.

The elongation figures are somewhat more variable than the tensile, but most relief-annealed tubes have appreciably higher elongations than the corresponding drawn or sunk tubes. The average for all 10 tubes indicates that relief annealing increases the elongation by approximately one-third.

The modulus of elasticity at zero load varies somewhat with the different tubes. The mean difference, however, between the drawn or sunk and the corresponding relief-annealed tubes is less than 100,000 lb. per sq. in., which is well within the experimental error. In fact, with a more precise extensometer probably the various tubes would have shown less variation in the modulus at zero load. The figures for rate of decrease of modulus of elasticity (sixth column of Table 2) are interesting and reflect the influence of the relief annealing.

Hardness Tests

The standard Rockwell hardness tester was used with $\frac{1}{16}$-in. ball, 100-kg. load and B scale. At least 10 readings were taken on each tube, both as drawn and as relief-annealed. Every precaution was taken to obtain as accurate results as possible. The drawn or sunk tube and the corresponding relief-annealed tube were tested one immediately after the other with identically the same test conditions. The differences due to relief annealing, though not great, are therefore felt to be quite reliable. The results of the hardness tests are included in Table 2.

The results on tubes 1 to 5 inclusive are interesting. This is a series with decreasing amount of sink. The tubes with greater amounts of sink, and therefore the greatest initial hardness, show a considerable increase in hardness on relief annealing. There is a fairly consistent lessening of this effect with decreasing amounts of sink. From published data we would expect this greater increase in hardness on relief annealing with the greater initial hardness. This was first shown quantitatively by Bassett and Davis[4] in 1919.

No great difference was shown between the type and degree of reduction of tubes 6 to 9 inclusive and the increase in hardness on relief annealing. A regularly decreasing change of outside surface hardness might have been expected in going from tube 6 to tube 9. The rather small change in tube 10 would be expected from a tube so drawn, as the stress should be low.

Mercurous Nitrate Tests

These tests were made in triplicate on samples cut to 3-in. length, which slightly exceeded the minimum found previously to give reliable results. Standard conditions of tests were used. The results are included in Table 2. Attention is called to the fact that all of the sunk tubes cracked in very short times, as was to be expected. The very short times for tubes 1 and 2 are probably not too accurate, as it takes nearly the time indicated to get the samples completely immersed and the reaction started.

The time required to crack for tubes 6 and 7 are about as might be expected from the type and severity of the draw. We might have expected tube 7 to require a somewhat longer time to crack than tube 6, but it must be remembered that the test is at best not too precise. The

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[4] W. H. Bassett and C. H. Davis: A Comparison of Grain-size Measurements and Brinell Hardness of Cartridge Brass. *Trans.* A.I.M.E. (1919) **60,** 428–449.

TABLE 2.—*Physical Properties*

Tube No.[a]	Maximum Stress, Lb. per Sq. In.	Elastic Limit, Lb. per Sq. In.	Elongation in 10 In., Per Cent	Modulus of Elasticity		Rockwell Hardness, 16-100-B	Change in Hardness by Relief Annealing	Time to Crack in $HgNO_3$ Soln., Min.
				At Zero Load, Lb. per Sq. In.	Rate of Decrease with Load[c]			
1-S	61,000	37,500	3.7	15.7[b]	0.41	80.0		0.32
1-A	59,900	37,500	6.3	15.7	0.21	84.0	+4.0	21.3
2-S	59,800	39,500	5.9	16.9	0.15	75.8		0.23
2-A	59,500	38,400	5.4	17.5	0.14	80.0	+4.2	13.6
3-S	59,600	36,000	10	17.5	0.28	73.3		0.38
3-A	58,700	34,500	13	17.5	0.20	76.4	+3.1	5.3
4-S	53,800	27,000	14	16.0	0.19	68.2		0.46
4-A	53,500	21,000	21	16.0	0.00	70.0	+1.8	[d]
5-S	47,300	20,000	27	15.8	0.41	67.3		0.53
5-A	48,700	16,500	30	15.8	0.16	66.5	−0.8	[d]
6-D	56,300	34,400	1.3	16.0	0.33	83.2		6.2
6-A	57,000	32,500	3.4	16.1	0.22	85.5	+2.3	[d]
7-D	62,200	45,000	6.2	17.0	0.82	79.7		3.7
7-A	61,600	45,000	5.9	17.0	0.46	81.6	+1.9	[d]
8-D	60,200	45,000	5.0	17.1	0.51	78.4		[d]
8-A	61,300	40,000	8.5	17.1	0.22	80.9	+2.5	[d]
9-D	63,700	41,500	6.0	17.5	1.06	81.7		4.9
9-A	61,600	47,000	10.0	17.5	0.52	82.9	+1.2	[d]
10-D	68,800	44,400	0.9	17.1	0.97	87.3		[d]
10-A	69,300	44,400	0.3	17.1	0.32	88.0	+0.7	[d]

[a] S = as sunk; D = as drawn; A = as relief-annealed.
[b] Multiplied by 10^6.
[c] Lb. per sq. in. × 10^6 per 10,000 lb. per sq. in. tensile load.
[d] These tubes did not crack in 1 hr.

tubes that did not crack (8 and 10) would not have been expected to. They had had a type of reduction that should give low stress, because of the relatively great wall reduction and light diameter reduction. Tube 9 should have behaved in the same way as 8 and 10. No explanation can be given for its abnormal reaction. But, as will be shown later, the stress in this tube was quite similar to that in No. 6, so that it really should have cracked as it did. Viewed from this angle its performance was perfectly normal.

MEASUREMENT OF STRESS

A review of the literature shows a number of different methods of estimating circumferential stresses in drawn tubes. They vary from very simple ones giving only an approximate idea of surface stress to quite involved ones supposedly giving exactly the distribution across the wall. For the purpose of comparing differently drawn tubes to explain their different resistance to season cracking and the mercurous nitrate test, it was desirable to have a relatively simple method, which would yet give a fair idea of the amount and distribution of such stresses. The method originally described by Heyn and Bauer[5] is not applicable to tangential stress. That described by Sachs[6] would involve an excessive amount of work as well as precision of measurement unattainable with instruments at hand. The same objection would hold for Dawidenkow's[7] method. On the other hand, it seemed that Hatfield and Thirkell's[8] method would give an insufficient idea of stress distribution. On the whole, the general procedure followed by Fox[9] seemed to hold forth the best combination of simplicity and fair accuracy.

In 1930 Fox published a very interesting and valuable contribution to the literature of internal stress distribution. He carried out experiments to show that circumferential stresses in a tube wall need not necessarily follow a straight line distribution. Any one of three types of distribution might be found, depending on precise conditions of drawing of the tube. He contended that the real criterion of tendency to season crack was the internal couple released by splitting and not the magnitude of stress at the surface layers. The couple released depended on the area under the curve.

Fox investigated the distribution of stress by turning off successive layers from both outside and inside surfaces and subsequently splitting rings from the tubes. He then measured the amount of spring of the rings in order to calculate the stress distribution. His whole argument rested on the assumption that there was a power function type of distribution across the wall; that is, the curves approximated to the form $f = \alpha t^n$. Although it was not apparent that such need necessarily be the case, the general ideas seemed logical and the method was one which necessitated only a degree of accuracy of measurement obtainable with good micrometer calipers.

The 10 tubes used for the experimental work in the previous experiments were used here also. Duplicate tests were run on each, making a total of 20 tubes actually investigated. The individual sections were machined with the greatest of care, removing successive layers 0.005 in. thick from both inner and outer surfaces. The tubes were split and the change in radius of curvature accurately measured.

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[5] E. Heyn and O. Bauer: Über Spannungen in kaltgereckten Metallen. *Int. Ztsch. f. Metallographie* (1911) **1**, 16–50.

[6] G. Sachs: Der Nachweiss innerer Spannungen in Stangen und Rohren. *Ztsch. f. Metallkunde* (1927) **19**, 352–358.

[7] N. Dawidenkow: Berechnung der Restspannungen in Kaltgezogenen Rohren. *Ztsch. f. Metallkunde* (1932) **24**, 25–29.

[8] W. H. Hatfield and G. L. Thirkell: Season Cracking. *Jnl.* Inst. of Metals (1919) **22**, 67–85.

[9] J. Fox: The Measurement of Initial Stresses in Hard-drawn Tubes. *Engineering* (1930) **129**, 65–67.

Following Fox's procedure, the change in mean radius of curvature was plotted as a function of the residual wall thickness in Fig. 5. A study of this figure shows essentially the same things found by Fox. In general, the hollow sunk tubes (1 to 5 inclusive) show a marked increase in amount of spring as the wall is reduced. However, in tubes 1, 2 and 3, which had the greatest amount of sink in the order given, the curve reverses sharply as the thinner wall thicknesses are approached. This was not reported by Fox. The drawn tubes (6 to 10 inclusive) show mostly a slightly decreasing amount of spring as the wall is thinned, with the exception of 9, which is quite constant. This checks with Fox's findings. Attention is called to the very great difference in *amount* of change of curvature for the sunk tubes as a group and the drawn tubes as another. This was not brought out by Fox.

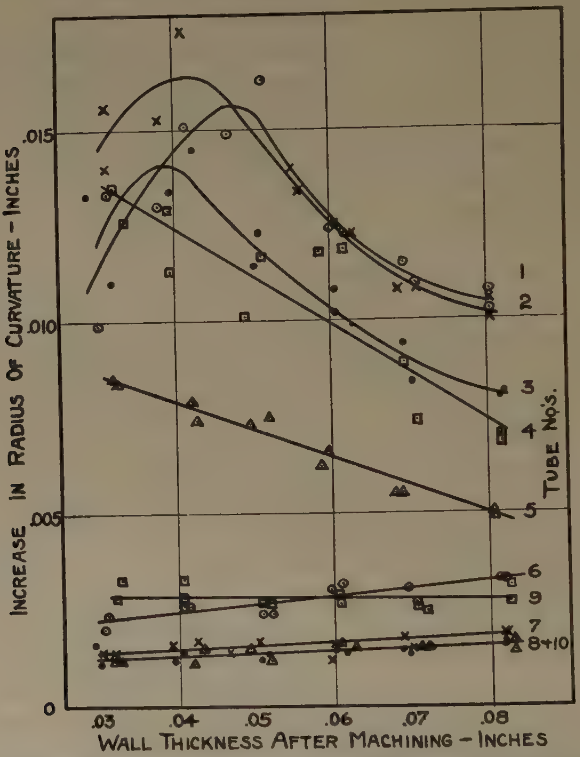

FIG. 5.—CHANGE IN RADIUS OF CURVATURE OF DRAWN AND SUNK TUBES AS A FUNCTION OF REMAINING WALL THICKNESS AFTER REMOVING EQUAL AMOUNTS FROM INNER AND OUTER SURFACES.

The next step in Fox's procedure was to plot the function $\frac{R_2 - R_1}{R_2} \times t$ as a function of t to get the value of the exponent n in his equation which follows:

$$f_c = \frac{(n + 2)E}{12\pi R_1} \times \frac{St}{R_2}$$

He assumed a stress distribution of the type $fc = \alpha t^n$. The constant n is, therefore, the slope of the straight line that should result from plotting the logarithms of the quantities involved. In Fig. 6 are shown such graphs for the 10 tubes tested. It is at once apparent that most of these are far from straight lines and that Fox's assumption as to type of stress distribution is erroneous. The study of Fig. 6 indicates that in particular the sunk tubes have stress distributions departing very appreciably from the form given by Fox. Where these curves were not straight lines as plotted on logarithmic paper attempts were made to straighten them by the usual procedure of adding a constant to all values of each variable independently, but the curves could not be so straightened.

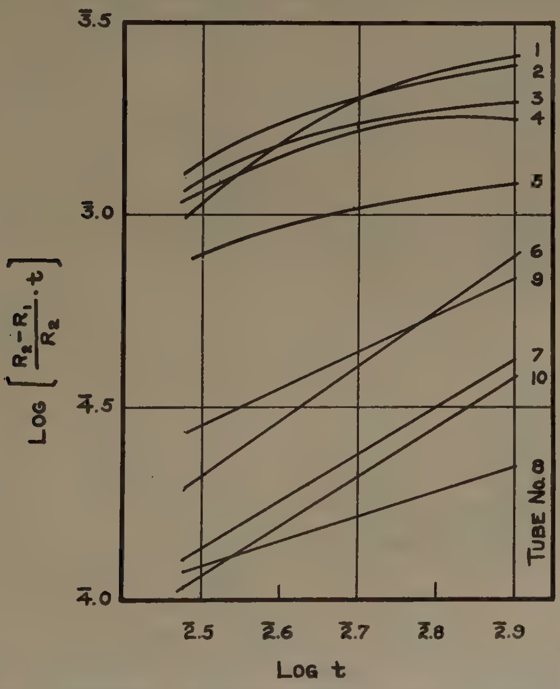

Fig. 6.—Relation between variable stress factor in Fox's equation and remaining wall thickness for all tubes.

In view of the inability to exactly check Fox's findings, a slight departure from his exact procedure was adopted. It was noted that Fox's equation for stress at a given point was very similar to Hatfield and Thirkell's. Both might be expressed in the form

$$S = K \times \frac{R_2 - R_1}{R_2} \times t.$$

Using Fox's procedure, identically the same shape of curve would be obtained as would result from applying Hatfield and Thirkell's formula to the various thicknesses of tubes machined from any one original tube. Where Fox's assumption as to stress distribution does not hold, as good an approximation to the *type* of curve would be obtained with the latter procedure as with Fox's own. Therefore, for each of the 10 tubes, curves were plotted for the stress obtained by Hatfield and Thirkell's formula as ordinates against the residual wall thicknesses as abscissas. Fig. 7 shows the curves so obtained for all 10 tubes. The individual plotted points are not shown, as they would be too confusing where the curves fall close together. It is not claimed that these curves show the actual stresses originally present. They do, however, give approximate indications of both the *type* of curve and relative intensities of stress in the different tubes. They serve adequately to differentiate between the various treatments and explain the results obtained with the mercurous nitrate test described earlier.

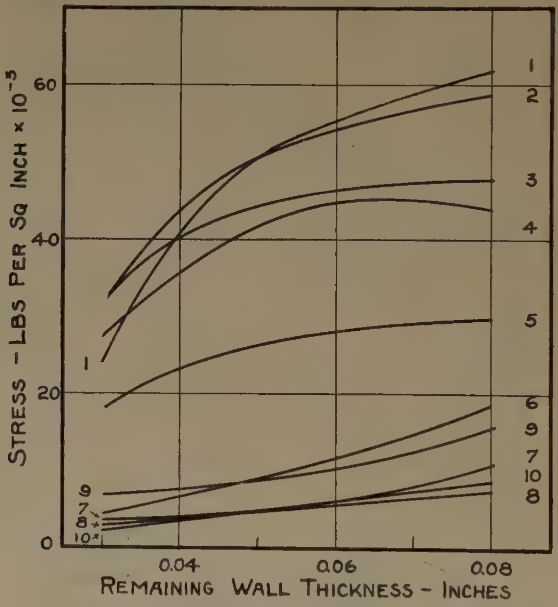

FIG. 7.—STRESS RELEASED BY SPLITTING AS A FUNCTION OF WALL THICKNESS REMAINING AFTER REMOVAL OF EQUAL AMOUNTS FROM BOTH INNER AND OUTER SURFACES.

The curves in Fig. 7 show the essential characteristics of *type* claimed by Fox. The sunk tubes (1 to 5 inclusive) are convex upwards. In other words, the stresses seem to persist in toward the center of the wall. The drawn tubes (6 to 9 inclusive) with intermediate area reductions show the opposite characteristic. Tube 10, which was drawn very hard with the least possible reduction of diameter, is a straight line, which also checks with Fox's work.

The general shape of curve seems to be as Fox described, in all cases. But there is a very important point not mentioned by Fox; namely, that the different shape of curve is also accompanied by markedly different stress intensity. Fox inferred that the season cracking of sunk tubes was due to the shape of the curve alone and the relative immunity of the drawn tubes to the different shape of their curves. On the basis of Hatfield and Thirkell's method, the difference in behavior would be explained entirely by the difference in surface stress. It is known that season cracks are progressive in nature. It seems probable that the initiation of such depends much on the intensity of surface stress and the rate of propagation on the shape of the curve. Both seem to be important and the present tests show that the dangerous type of distribution *is* usually accompanied by high stresses, and vice versa.

Stress in Single Crystals

Some preliminary tests on small single-crystal specimens of brass failed to result in cracks in the standard $HgNO_3$ solution, even though they had been so treated as probably to retain considerable internal stress. It would seem that there might be some question as to whether the failure to crack was due to lack of stress or simply to the lack of grain boundaries. It was thought worth while therefore to investigate the possibility of stress concentration at or near grain boundaries. A careful comparison of stress in single crystals and polycrystalline materials for identically the same treatment was the obvious way to determine such effect, if present.

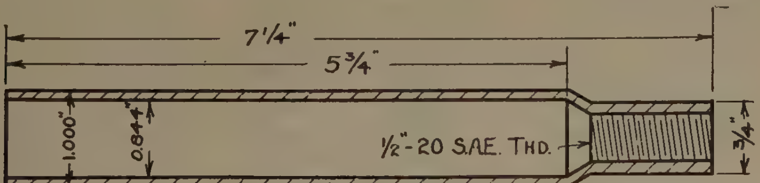

Fig. 8.—Type specimen used for comparing stress in single crystal and polycrystalline tubes.

Four large single crystals of high-grade 70-30 brass about 1⅜ in. in diameter and 7½ in. long were available. These were machined to the form and dimensions shown in Fig. 8. Procedure for machining was carefully worked out to avoid introduction of stress.

In order to get polycrystalline tubes for comparison, some annealed 70-30 brass rod sections 1⅜ in. in diameter and 7½ in. long were treated in precisely the same manner, resulting in machined tubes differing from the single-crystal tubes only in point of being polycrystalline. Four such tubes were made. The mean grain size of these tubes was about 0.070 mm.

In the first comparison test, two of the single-crystal tubes and two of the polycrystalline tubes were sunk through a ¾-in. die having a 20° angle and a ⅛-in. bearing. This work was done in a universal testing machine using a threaded steel rod to pull the tubes through the die. After sinking, only three good 2¼-in. long specimens could be obtained. Two were used for check determinations of the stress released using Hatfield and Thirkell's formula. The third was used for $HgNO_3$ immersion test.

In the second comparison test the other two single-crystal and polycrystalline tubes were used. The general procedure was the same except that the tubes were all drawn over a straight mandrel to the nominal size of 1³⁄₁₆ in. outside diameter by 0.075 in. wall. The mandrel was subsequently pulled out. With this light draw somewhat less stress would be expected than in the first comparison test. The summary of the surface stresses determined is given in Table 3.

TABLE 3.—*Stress in Single-crystal and Polycrystalline Tubes*
Stress Measured in Pounds per Square Inch

Tube No.	Sunk Tubes		Drawn Tubes	
	Single-crystal	Poly-crystalline	Single-crystal	Poly-crystalline
1*a*	42,200	45,200	23,000	34,500
1*b*	31,600	48,400	18,800	30,300
2*a*	36,000	44,300	20,800	28,800
2*b*	33,000	45,700	18,800	33,000
Average	35,700	45,900	20,500	31,700

Table 3 shows considerable variation in the several check tubes. However, this variation is decidedly less than the differences between the two types. In the sunk tubes the polycrystalline tubes show a mean stress 29 per cent greater than the single-crystal ones. In the drawn tubes this difference amounts to 55 per cent. It seems clear that these materially higher stresses can be explained only by assuming that there is in fact a concentration of internal stress at grain boundaries as postulated.

One section from each of the four single-crystal and polycrystalline tubes was subjected to the standard $HgNO_3$ test. The polycrystalline tubes, both sunk and drawn, cracked in 1 min. or less. None of the drawn or sunk single-crystal tubes cracked in 24 hr. Apparently it is impossible to so crack a single crystal, even though high internal stress is present. These tests show clearly that while there is a pronounced stress concentration at grain boundaries it is necessary also to have some specific corrosive action *at these boundaries* in order to produce season cracking.

LATTICE DISTORTION AND SURFACE HARDNESS

The considerable differences found in the previous part of our work under stress in various tubes led to a few interesting supplementary tests on effect of stress release on hardness. These tests were prompted by the work reported by Fink and Van Horn[10] on the effect of lattice distortion on hardness. These authors showed that when an external longitudinal tensile stress was applied to a strip by bending, a decrease in hardness of the surface resulted. In other words, stress and lattice distortion need not cause an increase in hardness; but under some conditions, a decrease. Evans[11] in discussing their paper said, "A tensile stress within the elastic range (as at the convex surface of a bent beam) will tend to increase the interatomic distance in the longitudinal direction and decrease the interatomic distance in the directions at right angles. Thus, although it should increase the hardness when measured axially, it should decrease it when measured laterally in the manner adopted by the authors, as indeed, they have found."

The logic of this reasoning is obvious. It would also follow that if the application of a tensile stress under the conditions stated resulted in a decrease in hardness, an applied compressive stress should cause an increase in hardness. Likewise, if a member is already stressed and that stress is released or removed, there should result an *increase* in hardness when the stress removed was tension and a decrease when the stress was compression.

In the tubes used there were tensile stresses at the outer surfaces and compressive stresses at the inner. The present tests were taken to show simultaneous increase in outer surface hardness and decrease in inner surface hardness when these stresses were released by splitting of the tubes. For this purpose sections of tubes 1, 6 and 10 were selected. Tube 1 had the greatest amount of sink and therefore the greatest stress. Tube 10 had the hardest draw, with the least reduction in diameter and therefore the least stress. Tube 6 had an intermediate type of reduction and intermediate stress.

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[10] W. L. Fink and K. R. Van Horn: Lattice Distortion as a Factor in the Hardening of Metals. *Jnl.* Inst. of Metals (1930) **44,** 241–248.

[11] U. R. Evans: Discussion of reference of footnote 10, 253.

In order to get accurate surface hardnesses on both inner and outer surfaces, special tools and fixtures were designed to go on the Rockwell machine. These will not be described at length, but it can be stated that very accurate tests could be obtained both before and after splitting such tubes. For each of the three tubes selected, 10 readings on each surface were taken, using the 100-kg. load, and similar tests made after splitting the tubes. In Table 4 the mean figure for the 10 closely agreeing check tests is given.

Table 4.—*Effect of Release of Stress by Splitting on Surface Hardness of Tubes*

Mean Figure for 10 Closely Agreeing Check Tests

	Tube 1		Tube 6		Tube 10	
	Outside	Inside	Outside	Inside	Outside	Inside
Before splitting	75.4	85.3	81.7	83.3	84.9	86.0
After splitting	79.9	83.8	83.9	82.5	84.7	86.2
Change	+4.5	−1.5	+2.2	−0.8	−0.2	+0.2

The results given here are precisely what were predicted by theory above. Also, the magnitudes of the changes are relatively as would be predicted. The slight changes found on tube 10 are not considered to be significant and probably represent about the limit of accuracy of the tests.

These simple comparison tests show that the increase in hardness usually reported on relief-annealed material is probably occasioned by the release or lowering of internal tensile stress by such anneals. If the stress released were compression a lowering of hardness would result. Where there is little or no stress released, no change in hardness follows. Also, the tests check the findings of Fink and Van Horn,[12] that lattice distortion need not necessarily produce hardening; but under certain conditions, softening.

X-RAY STRUCTURE

Recently Norton and Hiller[13] published interesting data on the effect of varying types of tube-drawing reductions on X-ray structure. These authors worked with mild steel tubes having a carbon content of 0.10 to 0.20 per cent. Sections were drawn to varying total area reductions and with varying relative amounts of diameter and wall reduction. They found that preferred orientation became apparent with total area reductions of about 20 per cent or more. In all cases the tendency was for a [110] axis to become aligned with the tube axis. If the percentage wall reduction were less than about twice the percentage diameter reduction, the orientation about the tube axis was random. This was similar to the structure obtained on drawn wire. When the ratio of wall reduction to diameter reduction exceeded about 2.5 to 1 it was found that a second [110] direction tended to become tangent to the tube wall. This structure was the same as found for rolled sheet.

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[12] Reference of footnote 10.

[13] J. T. Norton and R. E. Hiller: Structure of Cold-drawn Tubing. *Trans.* A.I.M.E. (1932) **99,** 190.

It seemed probable that in general similar structures might be found in the drawn brass tubes used in the earlier parts of this investigation. Among these were tubes of about as wide a range in ratio of wall reduction to diameter reduction as could possibly be obtained. Unfortunately, the total area reductions usually were not great enough to give a reasonable expectation of markedly preferred orientations. Three were selected for special study, Nos. 1, 8 and 10. The diameter, wall and area reductions for these three tubes were as shown in Table 5. For these, mean diameter reduction was used, as it seemed to be a more logical criterion than outside diameter reduction.

Table 5.—*Reductions for Tubes for X-ray Structure*

Tube No.	Area Reduction, Per Cent	Mean Diameter Reduction, Per Cent	Wall Reduction, Per Cent	Ratio Wall to Diameter Reduction, Per Cent
1	28	32	+8	−0.25
8	28	14	17	1.2
10	47	9	42	4.7

The same kind of "fiber diagrams" as taken by Norton and Hiller were made for each of these samples from each tube. The degree of preferredness as indicated by the intensity of the spots was not extreme in any case. In fact, in tubes 1 and 8, both of which had been reduced but 28 per cent, it was rather slight. In tube 10, which had been reduced 47 per cent, it was more marked.

The films for each of the three positions of each tube were carefully compared with "ideal" diagrams of all the probable orientations involving low indices. Most of these could be rejected immediately, as there was no correlation for at least one directional position. However, one orientation was found for tube number 1 and another for tubes 8 and 10 where reasonably good agreement was apparent between the films in each of the three directions and the corresponding "ideal" diagrams. The work of comparison was made difficult by the relatively slight degree of preferredness, especially in regard to tubes 1 and 8.

The type of preferred orientation found for the drawn tubes, 8 and 10, was such that a [111] direction coincided with the tube axis, a [110] direction was radial, and a [112] direction was perpendicular to the tube axis and parallel to a tangent to the tube surface. The type of preferred orientation indicated for tube No. 1 was such that a [112] direction coincided with the tube axis, a [111] direction was radial, and a [110] direction was perpendicular to the tube axis and parallel to a tangent to the tube surface. The orientations of the crystallites for these preferred orientations are shown in Figs. 9*a* and 9*b*.

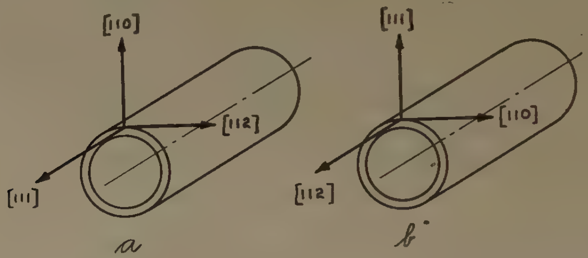

Fig. 9.—Crystallite orientation: (*a*) indicated by drawn brass tubes Nos. 8 and 10; (*b*) indicated by sunk brass tube No. 1.

These results are quite different from those reported by Norton and Hiller for iron. That there should be a difference in action between the two metals is not really surprising, as the two materials crystallize in different systems, as pointed out above. However, it is somewhat surprising that in the present case a different type of structure was found, depending on whether the tube was drawn or sunk, and apparently independent of the relative degrees of diameter and wall reduction. On the other hand, Norton and Hiller found a different type of structure with varying degrees of relative wall and diameter reduction more or less independent of whether the tubes were drawn or sunk. It seems probable that both materials might bear further investigation to check these differences. Also, it would be preferable to use the more exact (but more tedious and involved) method of pole figures described by Wever.[14]

While no attempt has been made to directly connect preferred orientations and internal stress, it seems probable that further work would show some such connection. Further work is contemplated in this direction. It is felt that certain preferred orientations might result in higher internal stress than others.

General Conclusions

1. Young's law of proportionality between stress and strain within the elastic limit does not hold directly for brass tubes drawn cold with

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[14] F. Wever: Texture of Metals After Cold Deformation. *Trans.* A.I.M.E. (1931) **93,** 51–75.

varying types of reduction. The modulus of elasticity is maximum at zero load and falls off continuously with increase in stress.

2. Relief-annealed tubes more nearly approach strict proportionality between stress and strain than do tubes not relief-annealed. It is probable that a perfectly relief-annealed tube would have a constant modulus of elasticity within the proportional limit.

3. Relief annealing has no effect on maximum strength of drawn tubes or on apparent elastic limit. It does, however, markedly increase surface hardness where the stress released was tension.

4. The time mercurous nitrate test gives a good indication of internal stress from drawing or sinking.

5. There appears to be no method for determining intensity and distribution of internal stress which does not require a degree of precision of measurement not easily attainable, or which is not very cumbersome and difficult to use, or which does not suffer considerably in accuracy. The method used here for comparing differently prepared tubes is admittedly only a first approximation. It does, however, serve adequately to differentiate between the various tube-drawing treatments and brings out clearly differences in both amount and distribution of circumferential stresses which can be correlated with the action in the mercurous nitrate test. In general, in hollow sunk tubes the stresses persist well into the tube wall, while in drawn tubes they fall off much more rapidly. In addition, the harmful type of stress distribution is accompanied by high surface stress, and vice versa.

6. There is considerable evidence that internal stresses in grain boundaries are materially higher than within the individual grains. At least polycrystalline tubes showed stresses from 29 to 55 per cent greater than identically treated single-crystal tubes.

7. There is a simultaneous increase of hardness of surface layers originally under tension and decrease of hardness of layers originally under compression when the stress is released by splitting. This shows that lattice distortion does not necessarily result in an increase of hardness, but under suitable conditions in a decrease.

8. The 70-30 brass tubes reduced 28 and 47 per cent in area by sinking or drawing show some evidence of preferred orientation. The type of preferredness in sunk tubes is such that a [112] direction is parallel to the tube axis, a [111] direction is radial, and a [110] direction tangential. In drawn tubes a [111] direction is parallel to the tube axis, a [110] direction is radial, and a [112] direction is tangential. These types of preferredness are different from those found by Norton and Hiller for mild steel tubes.

9. The possibility of some connection between type of preferred orientation and internal stress is suggested, and further work in this direction contemplated.

DISCUSSION

(*E. M. Wise presiding*)

E. M. Wise, Bayonne, N. J.—It is evident that an enormous amount of painstaking work has been done by the author, and the data are most welcome. It is particularly interesting to note the wide departure from linearity in the distribution of the stress with respect to the neutral axis, a possibility which I emphasized in discussing a previous paper by the author some years ago. A rather minor question may be raised as to the reason for simultaneous removal of metal from both the inside and the outside of the tubes for strain measurements, a procedure which perhaps complicates the computations of stress.

C. S. Barrett, Pittsburgh, Pa. (written discussion).—It seems to me to be a bit misleading to say, "It seems clear that these materially higher stresses [in polycrystalline as compared with single-crystal tubes] can be explained only by assuming that there is in fact a concentration of internal stress at grain boundaries as postulated." Surely the higher stresses in polycrystalline materials are not directly caused by stress concentrations at the grain boundaries. They result from the higher elastic limit of the polycrystalline material, and this is due, in turn, to slip interference at grain boundaries. To be sure, one would expect stress concentrations to occur at grain boundaries as a result of displacements of portions of the grains through slip, and these concentrations invariably to accompany internal stresses, but such concentrations should be considered a corollary rather than a cause of high stresses.

As to the cause for season cracking at grain boundaries, is there not ground for argument that it is the stress gradient rather than the magnitude of the stress? Probably the stress gradients as well as the stresses are greatest near the grain boundaries. It might be mentioned that another cause for inhomogeneity of stress lies in the marked elastic anisotropy of brass.[15] Only a few cubic materials have been studied from this standpoint, but among those studied brass has a particularly great variation in elastic modulus. One wonders if this anisotropy, which would produce local stresses and stress gradients of considerable magnitude whenever the grains were under externally applied stresses or residual stresses, would not make brass particularly susceptible to season cracking.

The author's conclusions from measurements of Rockwell hardness in stressed materials are readily granted if they are meant to refer only to the hardness as measured by a hardness tester. It cannot be doubted that tensile stresses aid the penetration of the Rockwell ball and compressive stresses oppose it. But it must not be inferred that this kind of experiment furnishes much evidence on *intrinsic* hardness of the material, the hardness in the absence of internal stresses. Any increase in resistance to slip on crystallographic planes due to lattice distortion, and the increase in intrinsic hardness caused thereby, would be submerged in the present experiment by the internal stresses present.

W. B. Price, Waterbury, Conn. (written discussion).—In discussing the relief-annealing of drawn brass tubes, the author makes the statement that "This anneal was carried out at 250° C. for 2 hr., a temperature and time that were found suitable from preliminary annealing tests on these tubes." The time, 2 hr., is in my experience not sufficient to completely remove internal stress. Moore and Beckinsale[16] have given a table showing the minimum times and temperatures in which injurious internal stresses were removed by low-temperature annealing, as follows:

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[15] Masima and G. Sachs: *Ztsch. f. Phys.* (1928) **50**, 161–186.

[16] Removal of Internal Stress in 70:30 Brass by Low-temperature Annealing. *Jnl.* Inst. Metals (1920) **23**, 232.

Temperature, Deg. C.	Time	Temperature, Deg. C.	Time
200	96 hr.	275	1 hr.
225	48 hr.	300	20 min.
250	5 hr.	325	5 min.

D. K. Crampton.—Mr. Wise asks if it would not have been preferable to remove all the metal from either the outside or inside in exploring stress distribution rather than from both surfaces simultaneously. There is something to be said for this, and in fact, for precise work, there is a distinct advantage. One very good reason for this is the fact that we are dealing with bending in a beam having considerable initial curvature. In dealing with ordinary rectangular cross-section beams initially straight, the neutral axis is in the exact geometric center and the stresses are a straight-line function from tension at one surface to an equal compression at the other. With tubes such as were used in the experiment described, we really have a rectangular beam of considerable initial curvature. Under such conditions the neutral axis is shifted appreciably towards the center of curvature and the stresses on the outer wall are lowered while those on the inner wall are raised compared to what would be found in the initially straight beam. Other difficulties that would be encountered in computation make this method of procedure less desirable and a compromise was made in this work between extreme accuracy and ease and economy of experimental procedure. The error introduced from this source does not seriously affect the general findings.

Dr. Barrett draws a rather nice distinction between what he terms "stress concentrations" and "internal stresses" at grain boundaries, a distinction that I am not sure is justified; in fact, in the original passage he discusses I used the term "internal stresses" in a broad sense to indicate the same general thing that I believe Dr. Barrett has in mind.

His remarks with respect to hardness are well founded. It was not intended that my remarks should be interpreted as referring to intrinsic hardness, although it appears from reading the text that such inference might readily be drawn. Perhaps instead of the word "hardness" the term "resistance to transverse penetration" would be more accurate.

Machinability of Free-cutting Brass Rod, II

By Alan Morris,* Bridgeport, Conn.

(New York Meeting, February, 1933)

In a previous paper[1] the results of cutting tests on free-cutting brass rod were reported. Investigation was made of the effects of variation in lead content, microstructure and cold drawing. The author's reply to the discussion of that paper includes a study of the directional cutting properties of drawn and annealed rod. The present paper records the results of tests made on series of samples in which the tin, iron and copper contents have been varied.

The apparatus used and method of testing are described in detail in the previous paper. The machine is of the pendulum-operated milling type used and described by Airey and Oxford.[2] Angular readings of the height to which the pendulum rises after falling from a fixed position, both when a cut is made and when the pendulum swings freely, give the basis for calculation of the energy consumed in making a cut. Careful weighing of the sample before and after cutting gives a measure of the amount of metal removed. The results are expressed in foot-pounds per cubic inch of metal removed, and have been called "unit cutting energy."

In the course of the discussion of the author's earlier paper, W. B. Price reported large-scale tests involving some 50,000 lb. of material. These tests indicated that the addition of as much as 0.6 per cent of iron and 0.25 per cent of tin had apparently no adverse effect on the high-speed cutting characteristics of the rod. The rod also contained a small amount of nickel. The test results reported here tend to confirm his observations.

Effect of Variation in Tin Content

The castings for this series were made 2 by 1 by 9 in. and were processed as follows:

1. Castings were annealed at 500° C. for 7 hr.
2. Cold-rolled to 0.700 in.

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* Research Engineer, Bridgeport Brass Co.

[1] A. Morris: Machinability of Free-cutting Brass Rod. *Trans.* A.I.M.E. (1932) **99**, Inst. of Metals Div., 323.

[2] J. Airey and C. J. Oxford: On the Art of Milling. *Trans.* A.S.M.E. (1921) **43**, 549.

3. Annealed at 500° C. for 8 hr.
4. Cold-rolled to 0.562 in.
5. Annealed at 500° C. for 2 hr. and air cooled.

Samples 1 by 2 by 0.562 in. were cut from the bars thus produced. Analysis, hardness and unit cutting energy are given in Table 1. Hardness and unit cutting energy are plotted against tin content in Fig. 1.

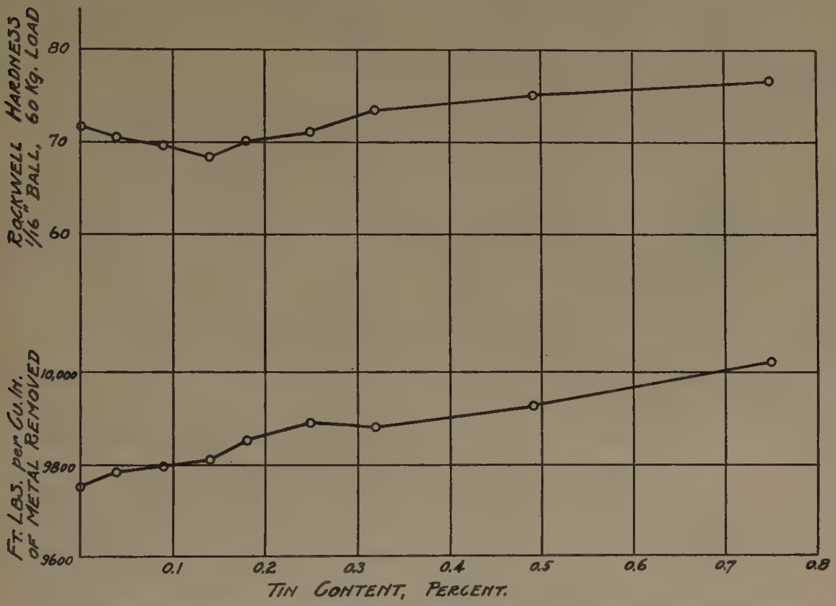

FIG. 1.—INFLUENCE OF TIN CONTENT ON HARDNESS AND UNIT CUTTING ENERGY.

TABLE 1.—*Data on Tin Series*

Sample No.	Analysis, Per Cent					Rockwell Hardness, 1/16-in. Ball, 60-kg. Load	Unit Cutting Energy, Ft.-lb. per Cu. In. of Metal Removed
	Cu	Pb	Sn	Fe	Zn		
1	61.06	3.18	None	0.01	Remainder	71.5	9,750
2	61.10	3.20	0.04	0.01	Remainder	70.5	9,780
3	61.14	3.19	0.09	0.01	Remainder	69.5	9,795
4	61.16	3.29	0.14	0.01	Remainder	68.5	9,810
5	61.03	3.19	0.18	0.02	Remainder	70.0	9,850
6	61.22	3.08	0.25	0.02	Remainder	71.0	9,890
7	60.77	3.24	0.32	0.05	Remainder	73.5	9,880
8	60.78	3.35	0.49	0.06	Remainder	75.0	9,920
9	60.90	3.16	0.75	0.04	Remainder	76.5	10,020

These curves indicate that the addition of tin up to 0.25 per cent has little effect on either the hardness or resistance to the cutting action of the tool. Further additions of tin, up to 0.75 per cent, cause a relatively small increase in hardness and resistance to cutting. Samples 7, 8 and 9 were made from stock containing more iron than that used in samples 1 to 6 inclusive. This may account for part of the rise in hardness shown by these three samples.

EFFECT OF VARIATION IN IRON CONTENT

Samples of leaded brass for these tests were prepared in the same manner as those for the tin series. In Table 2 are listed the analyses of the samples, together with the hardness data and unit cutting energy. Hardness and unit cutting energy are plotted in Fig. 2 as functions of iron content.

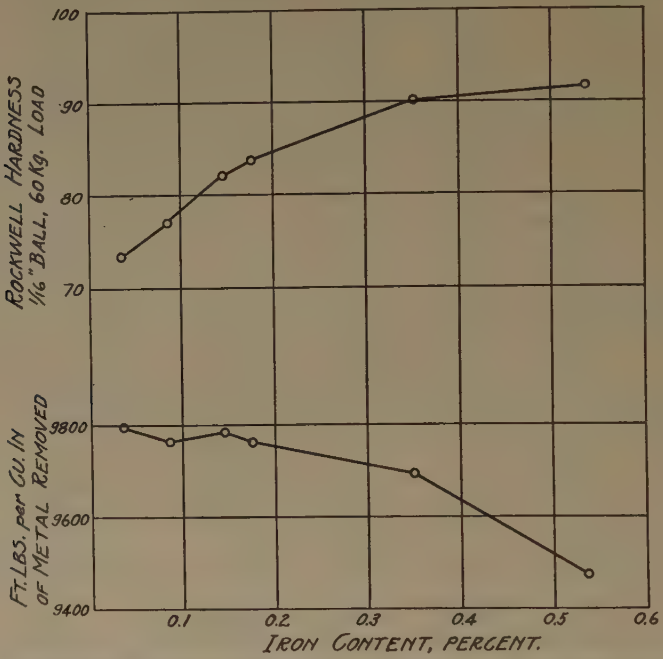

FIG. 2.—INFLUENCE OF IRON CONTENT ON HARDNESS AND UNIT CUTTING ENERGY.

TABLE 2.—*Data on Iron Series*

Sample No.	Analysis, Per Cent					Rockwell Hardness, $^1/_{16}$-in. Ball, 60-kg. Load	Unit Cutting Energy, Ft.-lb. per Cu. In. of Metal Removed
	Cu	Pb	Sn	Fe	Zn		
1	60.67	3.14	0.06	0.035	Remainder	72.5	9795
2	60.69	3.23	0.06	0.085	Remainder	77.0	9760
3	60.87	3.36	0.08	0.145	Remainder	82.0	9785
4	60.65	3.24	0.07	0.175	Remainder	83.5	9760
5	60.69	3.29	0.08	0.350	Remainder	90.0	9690
6	60.65	3.23	0.08	0.535	Remainder	91.5	9470

It appears that the addition of iron to the usual free-cutting brass rod alloy in amounts up to 0.5 per cent brings about a relatively small improvement in the cutting properties. However, the rod is also hardened materially, which is a disadvantage from the standpoint of mill production.

Effect of Variation in Copper Content

The castings for this series of samples were 1 by 2 by 9 in. and were prepared as follows:

1. Castings were annealed at 525° C. for 6 hr., furnace cooled.
2. Cold-rolled to 0.750 in.
3. Annealed at 525° C. for 6 hr., air cooled.
4. Cold-rolled to 0.500 in.

Two sets of samples were then prepared, one set for test as cold rolled, the other annealed at 500° C. for 2 hr. and cooled in silocel. In Table 3 are listed the analysis and unit cutting energy of each sample. These data are plotted in Fig. 3, and indicate that in the case of well homogenized material variation in copper content from about 58.0 to 63.0 per cent has very little effect on resistance to cutting. Increase in copper content from 63.0 to 65.0 per cent is accompanied by a moderate increase in unit cutting energy.

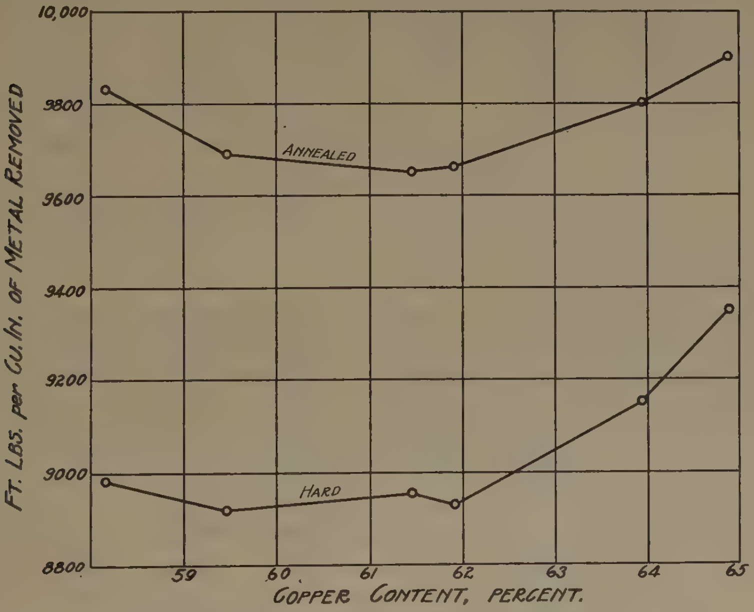

FIG. 3.—INFLUENCE OF COPPER CONTENT ON UNIT CUTTING ENERGY.

TABLE 3.—*Data on Copper Series*

Sample No.	Analysis Per Cent					Unit Cutting Energy, Ft.-lb. per Cu. In. of Metal Removed	
	Cu	Pb	Sn	Fe	Zn	As Cold Rolled	As Annealed
1	58.15	3.26	0.06	0.05	Remainder	8980	9830
2	59.46	3.24	0.07	0.05	Remainder	8920	9690
3	61 45	3.27	0.07	0.06	Remainder	8960	9650
4	61.90	3.27	0.06	0.05	Remainder	8930	9660
5	63.93	3.25	0.07	0.06	Remainder	9150	9800
6	64.87	3.25	0.06	0.05	Remainder	9350	9900

All cutting tests reported in this paper were made on the flat surface of the rolled sample, transverse to the direction of rolling. They correspond, therefore, to the "transverse" tests, as described in the author's reply to discussion on the previous paper.

All of the samples used were well homogenized, so as to eliminate the disturbing influence of beta as far as possible. No beta was found in any of the samples of the tin and iron series, and in the copper series only samples 1 and 2 contained beta. This degree of homogenization is of course not possible of attainment in present day mill practice, though it is often approached.

SUMMARY AND CONCLUSIONS

The results of cutting tests on three series of samples are reported, which indicate that:

1. Addition of tin up to 0.25 per cent has little effect on hardness or resistance to cutting. Further increase in tin content to 0.75 per cent causes moderate increase in hardness and unit cutting energy.

2. Additions of iron up to 0.5 per cent are accompanied by a moderate improvement in cutting properties, but cause material hardening.

3. In well homogenized material variation in copper content from 58.0 to 63.0 per cent has little effect on resistance to cutting. Increase of copper content from 63.0 to 65.0 per cent is accompanied by a moderate increase in unit cutting energy.

The Copper-rich Alloys of the Copper-nickel-tin System*

By John T. Eash,† Bayonne, N. J. and Clair Upthegrove,‡ Ann Arbor, Mich.

(Buffalo Meeting, October, 1932)

During recent years nickel has had an increasingly important role as an alloying element in the copper-tin bronzes. Nickel additions not only produce better casting alloys but also make alloys whose properties can be varied by precipitation hardening; thus leading to increased commercial application of copper-nickel-tin alloys.

Recent investigations have indicated a decrease in the solubility of tin in the alpha phase as the annealing temperature is lowered and as the nickel content is increased within certain limits. A further change caused by the nickel additions is produced in the excess phase of the copper-tin bronzes. The alpha plus delta eutectoid is replaced by a clear precipitated constituent in the alloys containing up to 15 per cent tin and not less than 1 per cent nickel.

This paper has a dual purpose. The first is to present a new determination of the alpha-phase boundary in alloys containing from 0 to 20 per cent nickel, together with the liquidus and solidus temperatures above that field. The second purpose is to give the equilibrium conditions existing in alloys exceeding the alpha phase containing up to 31 per cent tin and 5 per cent nickel, so that the disappearance of the alpha plus delta eutectoid constituent may be explained.

After considering the earlier investigations of the related alloy systems and the experimental procedure used in this investigation, the alloys will be discussed in groups as separate quasibinary systems containing constant amounts of nickel. The systems considered contain 0, 1, 2, 3, 5, 10 and 20 per cent nickel. The straight copper-tin system was reinvestigated in order to establish a foundation on which to build the remaining material. The 1 per cent nickel alloys studied give the relations existing in the region of the eutectoid transformation between the copper-tin system and the 2 per cent nickel copper-tin system which has been investigated in detail. The thorough examination of the latter system was made since 2 per cent of nickel is representative of the commercial additions to the cast bronzes and also because it is sufficient to produce decided changes in the copper-tin system. The 3 and 5 per cent nickel systems show the effect of increasing amounts of nickel on the equilibrium conditions. Only the alpha-phase boundary was determined for the 10 and 20 per cent nickel copper-tin systems.

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* Based on a dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Michigan.

† Metallurgist, Research Laboratory, International Nickel Co.

‡ Professor of Metallurgical Engineering, University of Michigan.

Review of Literature

The results of investigations of the copper-nickel, copper-tin, nickel-tin and copper-nickel-tin systems should be considered before considering the ternary system, because of the close relationships between the phases existing in the ternary system and those of the three binary systems.

The Binary Systems

Copper-nickel System.—Guertler and Tammann[1] published a diagram of this system in 1907. Copper and nickel form a complete series of solid solutions, as the metals are entirely miscible in one another in the solid state. The magnetic transformation, which is not accompanied by a structural change, is depressed by the addition of copper to room temperature at about 40 per cent of copper.

Copper-tin System.—The copper-tin system has been studied by many investigators because of its complicated phase transformations and the wide range of industrial applications of these alloys. Although the equilibrium conditions of this system have been the subject of a great amount of research, the equilibrium diagram is still in doubt. The main points pertinent to the present investigation in which the various diagrams disagree are (1) the solubility of tin in the alpha phase, (2) the nature of the horizontal at 590° C. and the beta inversion, (3) the formation of the alpha + delta eutectoid, (4) the composition of the delta phase. Bearing these points in mind, the results of the most important investigations of the copper-tin system are summarized in Table 1.

Nickel-tin System.—The nickel-tin system has not been the object of much investigation. In 1907 Guillet[2] developed a diagram showing an alpha solubility of 5 per cent tin. The entire system was made up of various solid solutions with a eutectic, at 64 per cent nickel, formed between the alpha and beta solid solutions.

A year later Voss[3] found that the alpha phase extended to 15 per cent tin. Unlike the previous work, the remaining phases consisted of a series of compounds of nickel and tin instead of solid solutions. A eutectic containing Ni_3Sn and alpha was formed at 69 per cent nickel. Both investigations showed a constant composition for the alpha boundary from the eutectic temperature to room temperature.

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[1] Guertler and Tammann: *Ztsch. f. anorg. Chem.* (1907) **52,** 25.

[2] Guillet: *Rev. de Mét.* (1907) 535.

[3] Voss: *Ztsch. f. anorg. Chem.* (1908) **57,** 38.

TABLE 1.—*Investigations of the Copper-tin System*

Investigator	Date	Solubility of Tin in Alpha Phase, Per Cent		Nature of Change at 590° C.	Eutectoid of Alpha + Delta Formed from	Composition of Delta Phase
		At Melting Point	At Room Temp.			
Heycock and Neville[a]	1903	9	9		Beta	Cu_4Sn
Shepherd and Blough[b]	1906	10	13		Beta	Solid solution (25–33% tin)
Hoyt[c]	1913	9	10	Beta to alpha + gamma	Gamma	Solid solution (27–32% tin)
Bauer and Vollenbruck[d]	1922	13.9	13.9	Beta to alpha + gamma	Gamma	Cu_4Sn
Isihara[e]	1924	10	11	Change in alpha	Beta	Cu_4Sn
Stockdale[f]	1925	13.3	16	Polymorphic		
Westgren and Phragmen[g]	1926					Solid solution over very small range. $Cu_{31}Sn_8$ is solvent. $a = 17.91$Å
Hansen[h]	1927	16 (518° C.)	14			
Raper[i]	1927			Polymorphic Change in the beta	Beta	Compound
Matsuda[j]	1928	15	15	Beta to alpha + gamma	Beta	Cu_4Sn
Carson[k]	1929	13 (16%, 520° C.)	15		Beta	Solid solution (32–33% tin)

References:

[a] Heycock and Neville: *Phil. Trans.* Roy. Soc. (1903) **202**, 1.
[b] Shepherd and Blough: *Jnl.* Phys. Chem. (1906) **10**, 630.
[c] Hoyt: *Jnl.* Inst. Metals (1913) **10**, 259.
[d] Bauer and Vollenbruck: *Ztsch. f. Metallkunde* (1923) **15**, 119–125, 191–195.
[e] Isihara: *Jnl.* Inst. Metals (1924) **31**, 315.
[f] Stockdale: *Jnl.* Inst. Metals (1925) **34**, 111.
[g] Westgren and Phragmen: *Ztsch. f. Metallkunde* (1926) **18**, 279–284.
[h] Hansen: *Ztsch. f. Metallkunde* (1927) **19**, 407.
[i] Raper: *Jnl.* Inst. Metals (1927) **38**, 217.
[j] Matsuda: *Sci. Repts.* Tohoku Imp. Univ. (1928) **17**, 144.
[k] Carson: *Canadian Min. & Met. Bull.* (Jan., 1929).

The Ternary System

Copper-nickel-tin System.—In 1928 Price, Grant and Phillips[4] published a diagram giving the 800° C. isotherm of the alpha-phase boundary. The solubility gradually decreased from 13 per cent tin and 0 per cent nickel to a minimum at about 8 per cent tin and 19 per cent nickel, and then increased to 15 per cent tin and 0 per cent copper on the high-nickel side of the diagram. The excess phase was considered to be beta in all cases.

In the discussion of that paper, Wise gave the alpha boundary at 800°, 700° and 300° C. for alloy compositions which range from 0 per cent nickel to approximately 40 per cent nickel. The 800° C. isotherm is practically the same as that given by Price, Grant and Phillips. At 700° C. the solubility is about 3 per cent less than at 800° C. At 300° C. the solubility decreased abruptly from 13.5 per cent tin and 0 per cent nickel to a minimum at about 2.5 per cent tin and 5 per cent nickel, followed by a gradual increase to 7 per cent tin and 40 per cent nickel. Wise found that, owing to the decrease in solubility between high and low temperatures, it was possible to age-harden alloys having compositions within this range.

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[4] Price, Grant and Phillips: *Trans.* A.I.M.E. (1928) **78**, Inst. Metals Div., 503.

In 1930 Upthegrove, Wilson and Rhines[5] published their results on the effect of small percentages of nickel on the hardness and microstructure of an 85 per cent copper and 15 per cent tin base alloy. The nickel was substituted for the copper, leaving the percentage tin constant. The addition of very small amounts of nickel did not produce any effect on the microstructure except to increase the percentage of eutectoid. With 1 per cent nickel two changes occurred. The alpha of the eutectoid disappeared and a dispersed constituent was found in the alpha. With increasing nickel content up to 10 per cent there was an increase in the amount and size of the dispersed phase.

In 1931 Pilling and Kihlgren[6] published the results of an investigation concerning the effects of nickel on the properties of a number of bronze foundry alloys.

EXPERIMENTAL PROCEDURE

Melting and Heat Treatment of the Alloys

The metals used in this study were electrolytic copper (99.96 per cent copper), Baker's C.P. tin and electrolytic nickel which was obtained from the International Nickel Co. The alloys used for the tests were melted in a Hoskins carbon resistor furnace. In the making of the melts of the copper-nickel-tin alloys an atmosphere of hydrogen was maintained at all times over the surface of the metal; 500-gram melts were used for the alloys. The fact was recognized that this type of alloy has a tendency towards inverse segregation, so great care was taken in melting and casting the alloys.

Table 2 gives the computed compositions of the alloys that were prepared. A sufficient number of alloys in each quasibinary system were analyzed to show that there was a very close agreement between the computed and analytical compositions of the alloys.

In order to anneal a large number of specimens at one time and to obtain a uniform temperature throughout a reasonable furnace length, an electric muffle furnace containing a copper block was used, patterned after the annealing furnace used by Dix and Richardson.[7] The furnace

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[5] Upthegrove, Wilson and Rhines: *Proc.* Amer. Soc. Test. Mat. (1930) **30,** 512–519.

[6] Pilling and Kihlgren: *Trans.* Amer. Foundrymen's Assn. (1931) **2,** 93–110.

[7] Dix and Richardson: *Trans.* A.I.M.E. (1926) **73,** 560–580.

TABLE 2.—*Computed Compositions of the Alloys*
Weight Per Cent

Nickel	Tin	Copper	Nickel	Tin	Copper	Nickel	Tin	Copper
0	14.5	85.5	3	1	96	10	7	83
0	15.5	84.5	3	1.5	95.5	10	8	82
0	16	84	3	2	95	10	9	81
0	17	83	3	3	94	10	10	80
0	27	73	3	4	93	10	15	75
0	31.8	68.2	3	5	92	10	18	72
			3	6	91			
1	27	72	3	9	88	20	2	78
1	28	71	3	10	87	20	3	77
1	29	70	3	11	86	20	4	76
1	30	69	3	11.55	85.45	20	5	75
			3	12.5	84.5	20	6	74
2	1	97	3	13.5	83.5	20	7	73
2	2	96	3	14.5	82.5	20	8	72
2	3	95	3	18	79	20	9	71
2	3.5	94.5	3	22	75	20	15	65
2	4	94	3	26	71	20	18	62
2	5	93	3	29	68			
2	6	92						
2	7	91	5	1	94			
2	8	90	5	1.5	93.5			
2	9	89	5	2	93			
2	10	88	5	3	92			
2	11	87	5	4	91			
2	11.5	86.5	5	7	88			
2	12	86	5	8	87			
2	12.5	85.5	5	9	86			
2	13	85	5	10	85			
2	13.5	84.5	5	11	84			
2	14.2	83.8	5	12	83			
2	15	83	5	13	82			
2	16	82	5	15	80			
2	18	80	5	18	77			
2	20	78	5	22	73			
2	22	76	5	26	69			
2	23	75	5	29	66			
2	24	74						
2	25	73	10	1	89			
2	26	72	10	1.5	88.5			
2	27	71	10	2	88			
2	29	69	10	3	87			
2	31	67	10	4	86			
			10	5	85			
			10	6	84			

temperature was controlled by an automatic controller and was held to ±2° C. during the annealing period.

No doubt one of the factors contributing to the wide variation in the position of the alpha-phase boundary and the location of other phase fields of the copper-tin system, as reported by previous investigators, was the length of time the alloys were annealed. The heating time used by various investigators has varied all the way from 45 minutes to 120 hours.

In the determination of the alpha-phase boundary in the present research, limiting points were found for temperatures of 780°, 700°, 500°, 300° C. and room temperature for each constant nickel percentage excepting the 1 per cent series. Sets of five or six samples of varying composition within which the boundary was expected to be found were placed in separate tubes in the copper block. All of them were initially annealed at 780° C. for 120 hr. At the end of that time the tube containing the alloys to be quenched at 780° C. was removed and quickly immersed in ice water. The furnace was then allowed to cool slowly to 700° C., where it was maintained for 24 hr. The tube containing the samples to be quenched at 700° C. was removed and quenched. The furnace was cooled to 500° C. and then to 300° C., where the same annealing time and quenching procedure was conducted in each case. A fifth set of samples was slowly cooled to room temperature. This method required approximately 130 hr. for the furnace to cool from 780° C. to room temperature, or a total time of 250 heating hours for the last set of samples.

In studying the phase changes occurring in alloys of high tin content a lower initial annealing temperature, 725° C., was used on account of the lower melting points of the alloys.

Thermal Analysis

The method of determining the melting points of the alloys is for the most part the same as described by Wood and Cork.[8] The samples, weighing approximately 175 grams, were cooled and heated at the rate of 3 to 5° C. per minute.

Thermal determinations of solid phase changes were made with the same apparatus, except that a bare thermocouple was fastened in a hole drilled into the center of the specimen. Specimens weighing 175 grams were heated and cooled at the rate of 3° C. per minute.

A second set of alloys was examined for thermal transitions in the solid state by means of a modified Rosenhain furnace. This procedure differed from the previous one in that the specimens weighed approximately 8 grams and were heated under a partial vacuum to eliminate oxidation. The samples were heated and cooled at the rate of 5° to 15° C. per minute.

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[8] Wood and Cork: Pyrometry, 167. McGraw-Hill Book Co. New York, 1927.

The specimens were homogenized by the annealing procedure described above, prior to the thermal analysis.

Polarized Light Examination

While microscopic examination under ordinary illumination was satisfactory in most cases, there was one phase, the delta prime constituent, which could not be distinguished by it. By using polarized light this phase could be identified.

By examining a polished metal surface under polarized light an isometric metal can be determined from one that is anisometric. For making these determinations a petrographic microscope equipped with two nicol prisms, one in front of the vertical illuminator and the other above it, was used. The unetched polished specimen was mounted on the stage of the microscope and an area selected under polarized light. The analyzing nicol was then slipped into the position of crossed nicols. If the metal or metal constituent was isometric it appeared dark and no change occurred on rotating the stage 360°. If an anisometric phase occurred, individual light and dark crystals were observed. On rotating the stage 90°, the light crystals turned dark and the dark crystals turned light. A 360° rotation caused two complete extinctions of the light crystals.

When plane polarized light is reflected from the polished surface of an isometric substance, its plane of vibration is not changed. Thus the reflected light will be extinguished when the analyzing prism is put in the position of crossed nicols.

With anisometric materials, however, the plane of vibration of the reflected light is rotated so that it has a component in the vibration direction of the analyzer and some light passes through. When the specimen is rotated under crossed nicols, the only positions in which the light is completely extinguished are when the principal directions of vibrations of the reflected light coincide with the vibration direction of the light from the polarizer.

According to Farnham[9] some metals and minerals will extinguish two times per revolution and others will extinguish four times. Antimony and stibnite, Sb_2S_3, are typical examples, respectively. In 1930 Heindlhofer and Bain[10] found that martensite gave four extinctions per revolution.

X-ray Measurements

Certain alloys were selected for analysis by means of X-rays in order to determine the nature of the phases present and also to measure their lattice parameters. The Debye-Scherrer or Hull powder method was employed, utilizing annealed filings.

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[9] Farnham: Determination of the Opaque Minerals. McGraw-Hill Book Co. New York, 1931.

[10] Heindlhofer and Bain: *Trans.* Amer. Soc. Steel Treat. (1930) **18,** 70–104.

The Copper-tin System

After considering the previous investigations of the copper-tin system, it can be seen that the results are diverse and that no two diagrams are exactly alike. Since the present study of the ternary system copper-nickel-tin was to be considered on the basis of quasibinary copper-tin systems containing constant amounts of nickel, it was necessary first to establish a copper-tin system around which the remainder of the work could be coördinated. Certain alloys were made and quenched at temperatures in the vicinity of some of the questionable points of the system; namely, the alpha-phase boundary, the gamma, gamma + beta, gamma + delta and delta fields.

The results obtained on the location of the alpha-phase boundary were in agreement with the Stockdale[11] diagram (Fig. 2). A specimen containing 15.5 per cent tin quenched at 590° C. contained only the alpha phase, while one containing 16 per cent tin consisted of alpha with a small amount of beta. On cooling the 16 per cent tin alloy to 500° C., all the beta dissolved in the alpha. Apparently there was an increase in solubility of tin in the alpha phase on cooling to the lower temperature. No doubt the increase in solubility stops at 520° C., the temperature of the beta prime to alpha + delta change, as indicated by Stockdale. This same alloy showed no change in appearance at 300° C. and room temperature. This would show that there is not a decrease in solubility on cooling below 500° C. A 17 per cent tin alloy contained alpha + beta at 590° C. and alpha + eutectoid (alpha + delta) at room temperature.

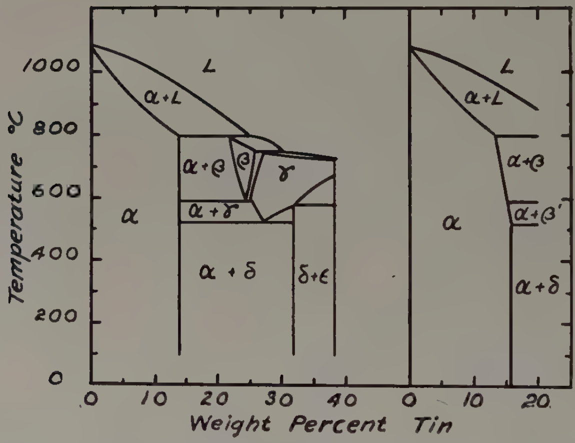

Fig. 1. Fig. 2.

Fig. 1.—Copper-tin system by Bauer and Vollenbruck.
Fig. 2.—Alpha-phase boundary of the copper-tin system by Stockdale.

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[11] Stockdale: *Jnl.* Inst. Metals (1925) **34,** 111.

The Bauer and Vollenbruck[12] diagram (Fig. 1) indicates a constant solubility of 13.9 per cent tin from 798° C. to room temperature, while the Stockdale and Carson[13] diagrams (Figs. 2 and 3) show an increase from about 13.3 to 16 per cent tin between 800° and 520° C. Stockdale indicates a constant alpha solubility from 520° to 25° C. and Carson a decrease from 16 to 15 per cent tin. The present work confirms Stockdale's diagram.

The alloy containing 27 per cent tin gave structures at various temperatures that are in agreement with the Bauer and Vollenbruck and Matzuda[14] diagrams. The alloys quenched at 725° and 572° C. were homogeneous. The entire specimens were made up of large polygonal crystals, which were dark brown on etching with acid ferric chloride. The Carson diagram would require that the alloy quenched at 725° C. be beta + gamma. On cooling to 500° C. the eutectoid (alpha + delta) with a trace of excess alpha was obtained (Fig. 4). No further change occurred on cooling to room temperature.

On quenching the 31.8 per cent tin alloy at 725° C. the gamma phase was obtained (Fig. 5). A trace of a second constituent, delta, can be seen at the grain boundaries. The gamma has a spotted appearance, which would indicate that it was on the verge of breaking down. Apparently the high tin gamma constituent is unstable and very hard to retain even under drastic quenching conditions. Carson observed the same phenomena in the alloys occurring in his gamma field.

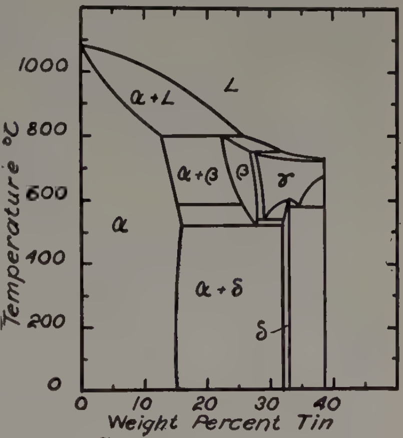

FIG. 3.—COPPER-TIN SYSTEM BY CARSON.

At 572° C. this same alloy contained gamma and delta phases (Fig. 6). The delta constituent formed in the grains and at the grain boundaries of the gamma phase. The gamma still had the spotted appearance. Both the Raper[15] and Bauer and Vollenbruck diagrams require that at 572° C. an alloy of this composition be 100 per cent delta. Carson found, however, that gamma and delta existed at this point in about the same proportions as shown in Fig. 6. The first two diagrams indicate that delta is a compound existing below 580° C., while Carson shows it to be a solid solution existing over the range 32 to 33 per cent tin at room temperature after forming directly from gamma containing 33 per cent tin at 610° C. This would allow for a wider gamma + delta field.

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[12] Bauer and Vollenbruck: *Ztsch. f. Metallkunde* (1923) **15,** 119–125, 191–195.

[13] Carson: *Canadian Min. & Met. Bull.* (Jan., 1929).

[14] Matsuda: *Sci. Repts.* Tohoku Imp. Univ. (1928) **17,** 144.

[15] Raper: *Jnl.* Inst. Metals (1927) **38,** 217.

At room temperature the 31.8 per cent tin alloy contained delta and a small amount of the alpha + delta eutectoid (Fig. 7). This further confirmed Carson's work that delta is not the compound Cu_4Sn, which contains 31.8 per cent tin. The results of work on the ternary system also indicate that delta is a solid solution.

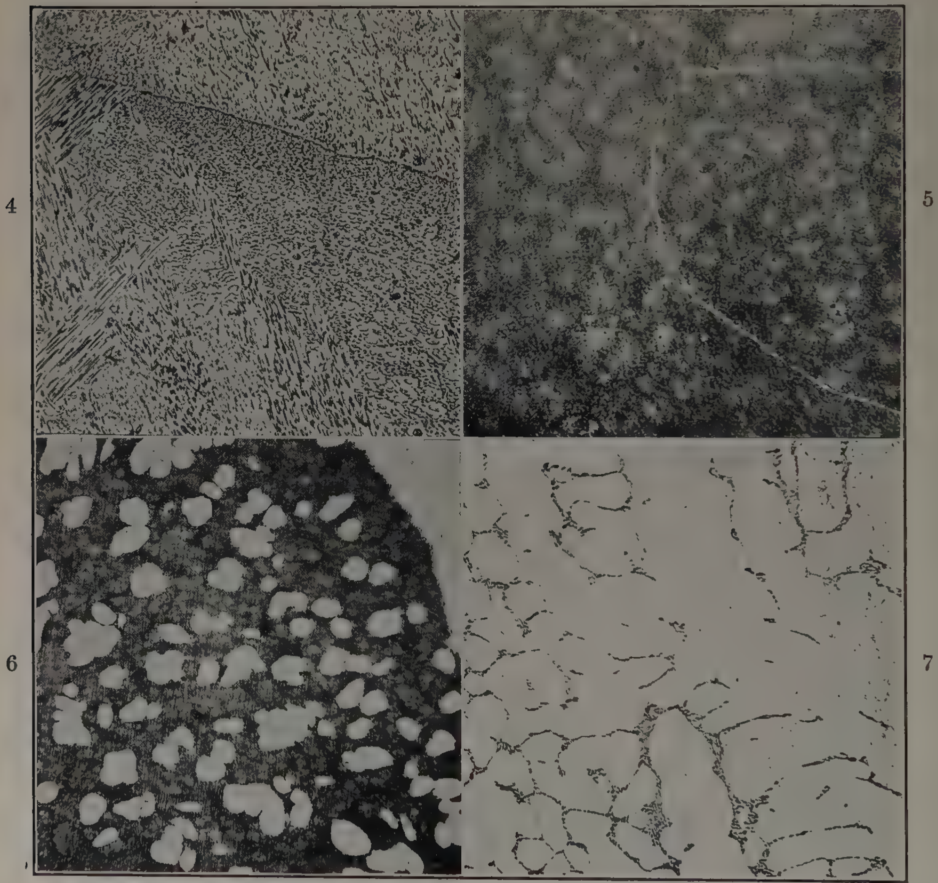

FIG. 4.—TIN, 27; COPPER, 73 PER CENT. QUENCHED AT 500° C. EUTECTOID (ALPHA + DELTA).
FIG. 5.—TIN, 31.8; COPPER, 68.2 PER CENT. QUENCHED AT 725° C. GAMMA.
FIG. 6.—TIN, 31.8; COPPER, 68.2 PER CENT. QUENCHED AT 575° C. GAMMA + DELTA.
FIG. 7.—TIN, 31.8; COPPER, 68.2 PER CENT. COOLED TO ROOM TEMPERATURE. EUTECTOID (ALPHA + DELTA) + DELTA.
ALL × 100. ALL ETCHED WITH ACID FERRIC CHLORIDE.

After considering the results described above, it can be seen that while various parts of the different diagrams agree with them, no one diagram does. This would suggest the putting together of parts of the diagrams to make a copper-tin diagram which agrees entirely with the present results on that system and also the ternary system. With this in mind the diagram shown in Fig. 8 was constructed. The alpha solubility from 0 to 16 per cent tin was taken from Stockdale's diagram. The solid phase changes from 16 to about 31.7 per cent tin were taken from the Bauer and Vollenbruck diagram. This part of the diagram indicates that the beta in alloys from 15.5 to 25 per cent tin changes to alpha + gamma at 590° C. While the results obtained on just the one alloy containing 27 per cent tin are by no means sufficient to establish this region, the results from the ternary alloys indicate that this diagram is more closely related to the ternary system than either the Raper or Carson diagrams. Above 31.7 per cent tin the Carson diagram was used.

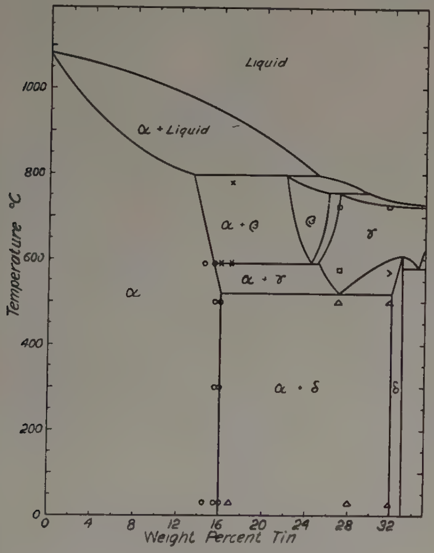

FIG. 8.

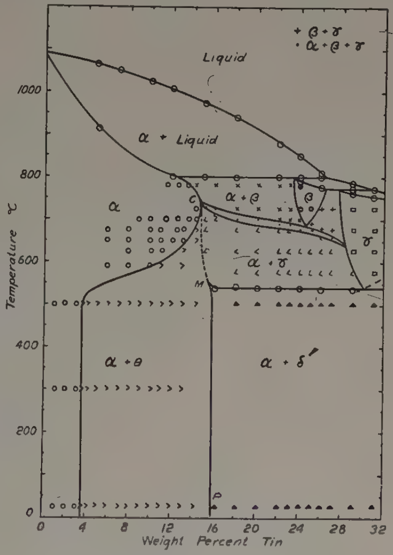

FIG. 9.

FIG. 8.—COPPER-TIN SYSTEM DERIVED FROM DIAGRAMS IN FIGS. 1, 2 AND 3. Points are shown which have been checked by the present authors.
FIG. 9.—THE 2 PER CENT NICKEL COPPER-TIN SYSTEM.

In the following discussion of the ternary alloys, any reference to the copper-tin system refers to this constructed diagram, Fig. 8.

THE TWO PER CENT NICKEL COPPER-TIN SYSTEM

The 2 per cent nickel copper-tin system was investigated quite extensively because this amount of nickel was sufficient to produce decided changes in the microstructure and was small enough to be representative of the effects produced by the addition of small amounts of nickel to the commercial copper-tin bronzes. The equilibrium diagram of this system is shown in Fig. 9.

Liquidus and Solidus.—The liquidus and solidus temperatures that were determined are recorded in Table 3. In the diagram shown in Fig. 9, the liquidus has been extended to 1090° C. at 0 tin which was taken from the copper-nickel diagram by Guertler and Tammann.[16] The present data connect very well with that temperature.

TABLE 3.—*Liquidus and Solidus Temperatures*

Ni, Per Cent	Sn, Per Cent	Solidus	Liquidus	Peritectic
2	5	913	1065	
2	7	.....	1047	
2	10	799	1021.7	
2	12	797.5	1001.5	
2	15	798.8	971.5	
2	18	797.3	934	
2	22	800	877	
2	24	789	848	801
2	26	774	809	798
2	29	764	782.5	772.5
2	31	756.5	772.5	764.8
3	6	901	1066	
3	9	796.5	1032	
3	12.5	796.	1003.5	
3	14.5	799.5	982	
3	18	799	939.5	Solid-solid trans.
5	7	841	1067.5	801.2
5	12	818.5	1022.5	799.8
5	15	812	990	
5	18	810.5	955	
10	7	899	1096	
10	10	875	1072.5	
10	15	858	1021	
10	18	860.5	991.5	
20	7	973	1139	
20	9	926	1132.5	
20	15	936	1072.5	
20	18	936	1038.5	

A comparison with the liquidus curves of the copper-tin systems by Stockdale[17] and Bauer and Vollenbruck[18] shows that 2 per cent nickel raised the liquidus temperature 14° C. (average) between 5 and 18 per cent tin. Between 18 and 26 per cent tin the increase was a little higher, averaging 21° C.

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[16] Reference of footnote 1.

[17] Reference of footnote 11.

[18] Reference of footnote 12.

The solidus horizontal extending from 12 to beyond 26 per cent tin was found to be at 799° C. Apparently the nickel has had no effect on this transition, for Stockdale as well as Bauer and Vollenbruck gave 799° and 798° C. respectively as the temperature of the solidus horizontal in the copper-tin system. A comparison of the copper-tin and 2 per cent nickel quasibinary systems shows that 2 per cent nickel has increased the tin contents of the beta, gamma and liquid phases that are in equilibrium with one another at corresponding temperatures.

Alpha-phase Boundary.—The increase in alpha solubility, as shown in Fig. 9, on cooling from 799° to 750° C. must be associated with a solute which is related to the beta phase. On cooling to between 750° and 700° C. the beta began to change to gamma, which in itself was an unstable constituent. As the gamma formed, the atoms of the alpha must likewise have changed their arrangement to some other form. When this occurred, insoluble nuclei were formed and an excess phase was precipitated if the tin content exceeded that of the alpha boundary. The precipitated phase has been designated as theta. The reasons for considering this a new phase will be explained later. The addition of 2 per cent nickel caused a decrease of more than 12 per cent tin in the alpha solubility at 25° C. compared to what it is in the simple copper-tin system.

The X-ray pattern obtained for a 12 per cent tin alloy containing 2 per cent nickel that had been annealed and quenched at 780° C. was typical of a face-centered cubic structure. The lattice constant computed from the measurements was 3.680 Å.

An interpolation of the values reported by Weiss[19] on the alpha phase of the copper-tin system for a 12 per cent tin alloy gives 3.673 Å. This is only 0.007 Å less than the above value. This shows that the addition of 2 per cent nickel has produced very little effect on the lattice parameter of the alpha phase.

Alpha + Beta Field.—The beta constituent was not retained in a homogeneous state even under very drastic quenching conditions. There was always a narrow blue band around it due to a partial decomposition. In the specimens containing small amounts of beta, the bands were more pronounced than in those containing large amounts, as can be seen by comparing Figs. 11, 14 and 15. Apparently the stability of the beta increased with the quantity present. It can also be seen that as the degree of supersaturation of the beta diminished, the tendency for the formation of the transition boundaries on quenching decreased. The alloys quenched at 780° C. contained more of the border effect than those

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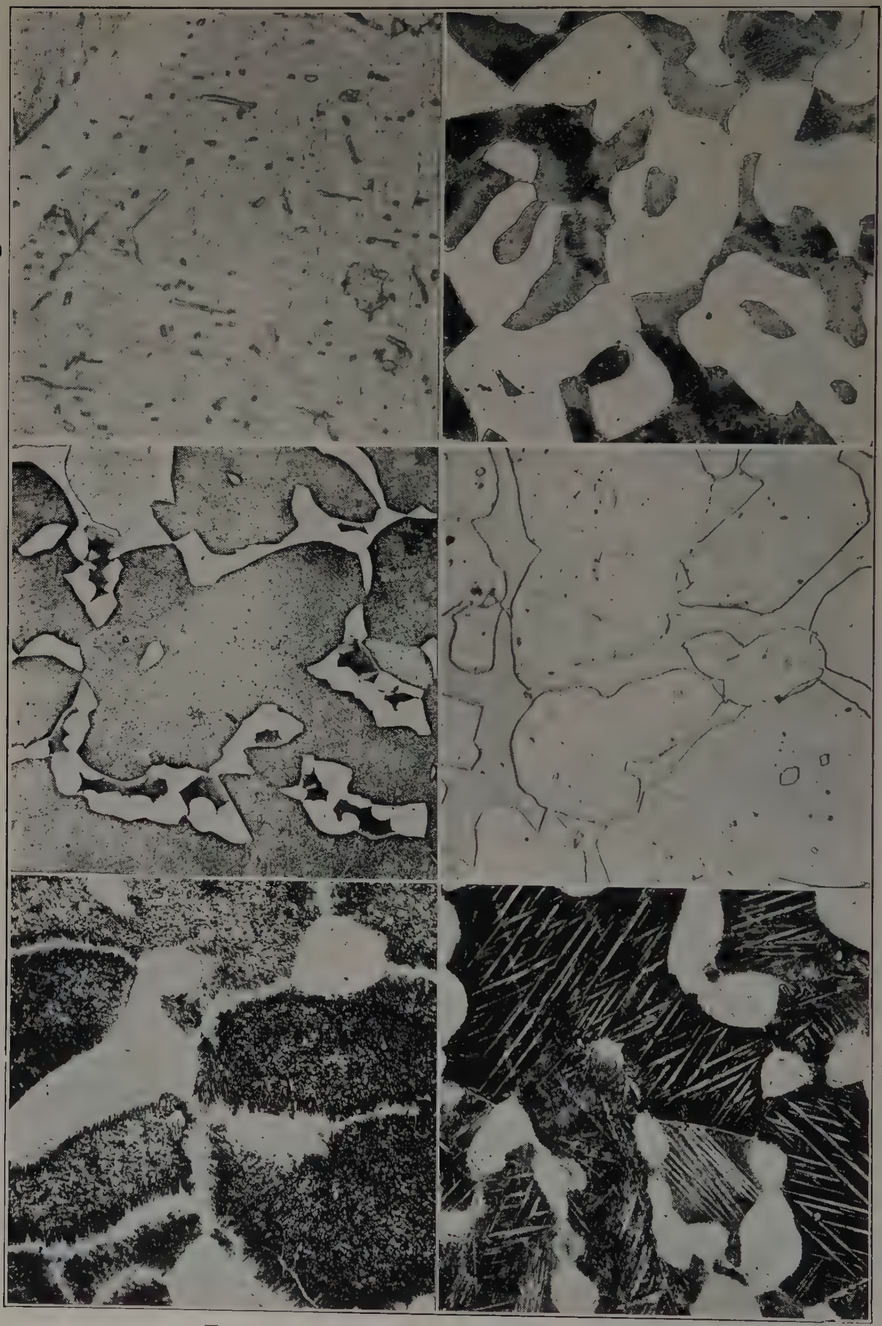
[19] Weiss: *Proc.* Roy. Soc. (1925) **108A, 643–654.**



Figs. 10–15.—Captions on opposite page.

quenched at 725° and 700° C. Stockdale observed this reaction rim around the beta phase in his study of the alpha + beta alloys of the copper-tin system.

Beta Field.—On comparing the beta field with that of the copper-tin system in Fig. 8, one can see that the presence of 2 per cent nickel caused a pronounced decrease in its size and a rise in the inversion point to alpha + gamma from 587° C. to 685° C.

The X-ray measurements of the beta constituent showed that the nickel addition caused an increase in the lattice parameter. A lattice constant of 2.994 Å was obtained for the 25 per cent tin alloy quenched at 725° C. Neuburger[20] gives the constant for a 15 atomic per cent tin (24.8 weight per cent) alloy quenched from the beta field to be 2.972 Å. Patterns typical of body-centered cubic crystals were obtained in both investigations.

Beta + Gamma Field.—There is a decided change in the shape of the beta + gamma field. Whereas in the copper-tin system it decreases in width from 1 per cent tin at 755° C. to less than 1 per cent at 587° C., in the 2 per cent nickel copper-tin system it increases in width from about 1.3 per cent tin at 773° C. to more than 3 per cent at the lower boundary. Both the upper and lower boundaries are raised in temperature.

The alloys in this area exhibited a peculiar flowerlike structure. In an alloy containing 26 per cent tin, quenched at 725° C., the gamma had separated at the edges of the beta grains in long crystals and in the beta grains in irregular sharp-cornered particles. On cooling this alloy to 675° C., the amount of the gamma increased so that it tended to form borders around the beta grains (Fig. 21). The interior particles increased in size and lost some of their sharpness and irregularity. In both cases the beta had a striated appearance.

The striations in the beta look like slip bands in that they are fine lines running in parallel directions in individual grains. These striations were probably caused by an internal strain in the beta grains. They could be due either to the quench itself or to a precipitation of the gamma

FIG. 10.—NICKEL, 2; TIN, 10; COPPER, 88 PER CENT. QUENCHED AT 300° C. ALPHA + THETA. × 1000.

FIG. 11.—NICKEL, 2; TIN, 18; COPPER, 80 PER CENT. QUENCHED AT 780° C. ALPHA + BETA (BLACK). × 100.

FIG. 12.—NICKEL, 2; TIN, 18; COPPER, 80. QUENCHED AT 700° C. ALPHA (GRAY) + BETA (BLACK) + GAMMA (WHITE). × 100.

FIG. 13.—NICKEL, 2; TIN, 20; COPPER, 78 PER CENT. COOLED TO ROOM TEMPERATURE. ALPHA + DELTA PRIME. × 100.

FIG. 14.—NICKEL, 2; TIN, 22; COPPER, 76 PER CENT. QUENCHED AT 780° C. ALPHA + BETA (BLACK). × 100.

FIG. 15.—NICKEL, 2; TIN, 22; COPPER, 76 PER CENT. QUENCHED AT 725° C. ALPHA + BETA (ACICULAR). × 100.
Etched with acid ferric chloride.

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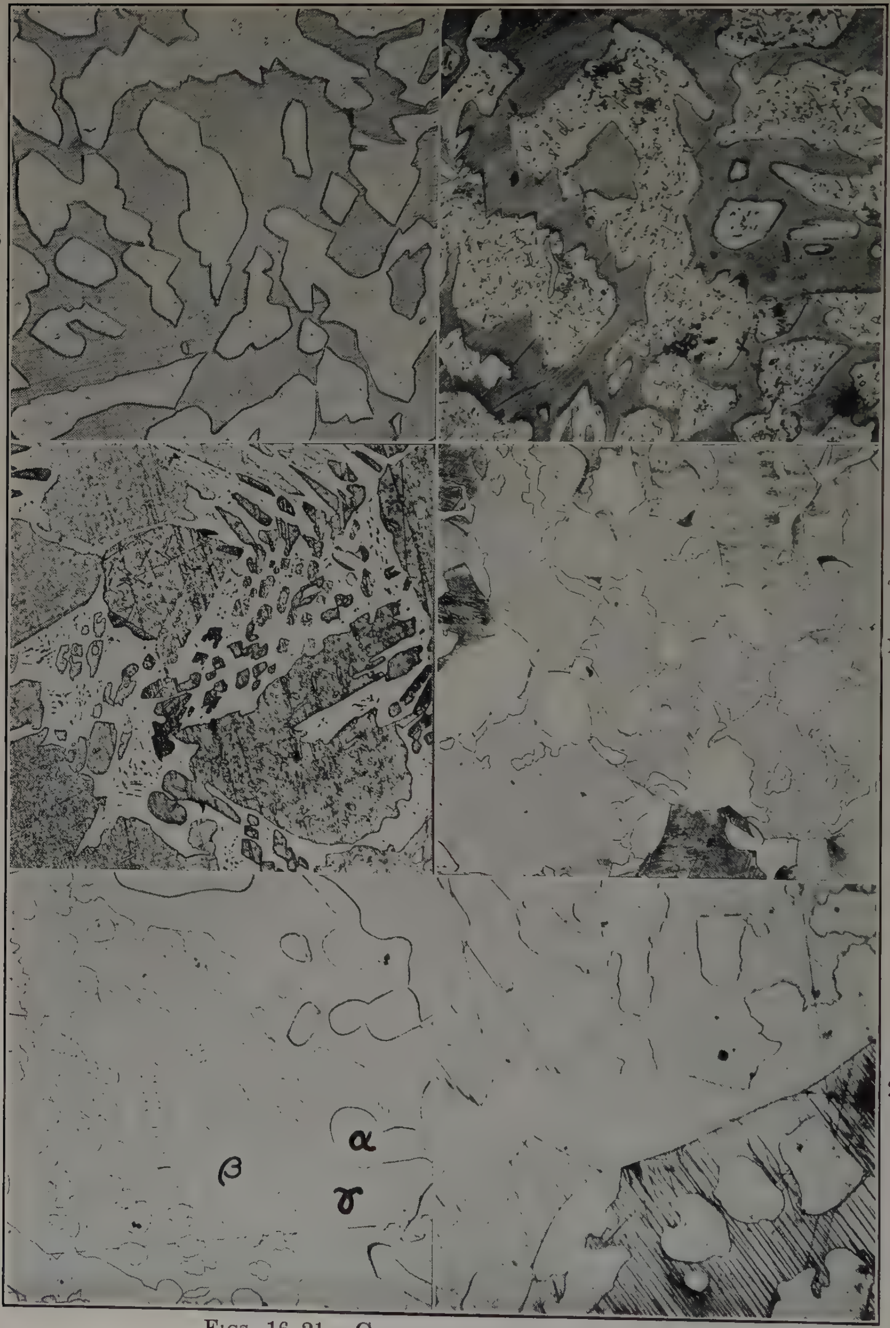
[20] Neuburger: Röntgenography of the Metals and Their Alloys, 144–151. F. Enke. Stuttgart, 1929.



Figs. 16–21.—Captions on opposite page.

phase along the crystal planes. The latter cause would seem to be the more probable.

Alpha + Beta + Gamma Field.—The beta change at 587° C. in the copper-tin system was raised to 750° C. at the high copper side and to 640° C. at the tin-rich side by the addition of 2 per cent nickel. Hoyt believed that the change at 590° C. in the copper-tin system was due to a transformation of the beta to alpha + gamma. This effect appears to have been accentuated by the presence of 2 per cent nickel, for a narrow field approximately 17° C. in width instead of a line was found to exist between 18 and 25 per cent tin. Below 18 and above 25 per cent tin the area diminished in width to 0° C. at 14.5 and 28 per cent tin respectively.

Fig. 12 shows the three phases obtained by quenching an 18 per cent tin alloy at 700° C. On comparing this with Fig. 11, it can be seen that the beta has almost completely changed to gamma. Fig. 19 shows the beginning of the gamma formation in the beta phase, which is partially striated. In a 24 per cent tin alloy quenched at 675° C., the beta + gamma phases had the flowerlike structure of the alloys occurring in the beta + gamma field and the alpha occurred as lozenge-shaped grains (Fig. 20).

From these observations it can be seen that the beta change occurring in this range is not a transformation to a eutectoidal structure of alpha + gamma, but merely a change to these two phases by a two-stepped transformation. First, the beta changes to gamma, which has a lower solubility for copper than the beta. Second, owing to this decrease in copper solubility in the gamma phase, there is a migration of the atoms and the alpha phase, which is copper rich, is precipitated. The alpha is always precipitated at the grain boundaries of the gamma and never between beta and gamma grains, where the differences in composition between the two phases tend to adjust themselves.

The beta change at 587° C. in the copper-tin system may well be the same kind of transformation. In the absence of nickel, the change occurs at a more rapid rate.

Gamma Field.—The 29 per cent tin alloys that were quenched at temperatures within the gamma field were homogeneous. The 31 per cent tin alloys, however, were of an unstable nature, as those that were

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FIG. 16.—NICKEL, 2; TIN, 22; COPPER, 76 PER CENT. QUENCHED AT 675° C. ALPHA + GAMMA (DARK). × 100.

FIG. 17.—NICKEL, 2; TIN, 22; COPPER, 76 PER CENT. QUENCHED AT 575° C. ALPHA + GAMMA (DARK). × 100.

FIG. 18.—NICKEL, 2; TIN, 22; COPPER, 76 PER CENT. COOLED TO ROOM TEMPERATURE. ALPHA + EUTECTOID (ALPHA + DELTA PRIME). × 100.

FIG. 19.—NICKEL, 2; TIN, 23; COPPER, 75 PER CENT. QUENCHED AT 688° C. ALPHA (WHITE) + BETA (DARK) + GAMMA (IRREGULAR SHAPED). ×100.

FIG. 20.—NICKEL, 2; TIN, 24; COPPER, 74 PER CENT. QUENCHED AT 675° C. ALPHA + BETA + GAMMA. × 100.

FIG. 21.—NICKEL, 2; TIN, 26; COPPER, 72 PER CENT. QUENCHED AT 675° C. GAMMA + BETA (STRIATED). × 100.

Etched with acid ferric chloride.

quenched above 625° C. contained a small quantity of precipitated delta prime. The alloy quenched at 575° C. was homogeneous. These same phenomena were observed by Matsuda[21] in his study of the copper-tin alloys.

Several attempts were made to obtain X-ray diffraction patterns of 31 per cent tin alloys quenched at 725° C. Very poor patterns were obtained and sometimes no definite lines were found after 12 hr. exposure. The unstable condition of the gamma constituent caused diffuse lines. This same phenomenon was observed by Carson in his work on the gamma phase of the copper-tin system.

Alpha + Gamma Field.—One of the most striking characteristics of the alloys occurring in this field was the variation in appearance of the gamma phase. At the high temperatures near the alpha + beta + gamma boundary the gamma phase had a light blue color after etching with acid ferric chloride, while at temperatures near the lower boundary it was dark blue. This is illustrated in Figs. 16 and 17. The same was true with the variation of the tin content. As the tin increased, the gamma changed from a light blue color to a dark blue-brown color.

The lower boundary of the field was determined by thermal examinations of seven alloys varying in tin content from 16 to 29 per cent tin. The thermal changes varied within the limits of 537° to 542° C., indicating a gamma eutectoid inversion at 539° C.

Alpha + Theta Field.—The theta constituent was clear and had a light blue color on etching with acid ferric chloride. It had a nodular and needlelike form, as is shown in Fig. 10 (a 10 per cent tin alloy quenched at 300° C.). While most of it occurred as a precipitated phase in the alpha, some of it is also located at the grain boundaries.

The theta constituent was considered to be different from the gamma phase, for the following reasons. A thermal examination of a homogenized 14.2 per cent tin alloy did not indicate any change between 500° and 650° C. This would indicate that the same phase was present from temperatures just below the alpha-phase boundary to below 500° C. The addition of 2 per cent nickel raised the temperature of the gamma inversion to

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FIG. 22.—NICKEL, 2; TIN, 27; COPPER, 71 PER CENT. COOLED TO ROOM TEMPERATURE. ALPHA + EUTECTOID (ALPHA + DELTA PRIME). × 100.

FIG. 23.—NICKEL, 5; TIN, 29; COPPER, 66 PER CENT. COOLED TO ROOM TEMPERATURE. ALPHA + DELTA PRIME (WHITE). × 100.

FIG. 24.—NICKEL, 2; TIN, 20; COPPER, 78 PER CENT. COOLED SLOWLY TO ROOM TEMPERATURE. REHEATED AND COOLED THROUGH 539° C. AT A RATE OF 10° C. PER MINUTE. ALPHA + EUTECTOID (ALPHA + DELTA PRIME). × 1000.

FIG. 25.—NICKEL, 5; TIN, 13; COPPER, 82 PER CENT. COOLED TO ROOM TEMPERATURE (COOLED FROM 700° TO 500° C. IN 10 HR.). ALPHA + THETA. × 100.

FIG. 26.—NICKEL, 20; TIN, 9; COPPER, 71 PER CENT. COOLED TO ROOM TEMPERATURE (COOLED FROM 725° to 500° C. in 94 HR.). ALPHA + THETA. × 1000. Etched with acid ferric chloride.

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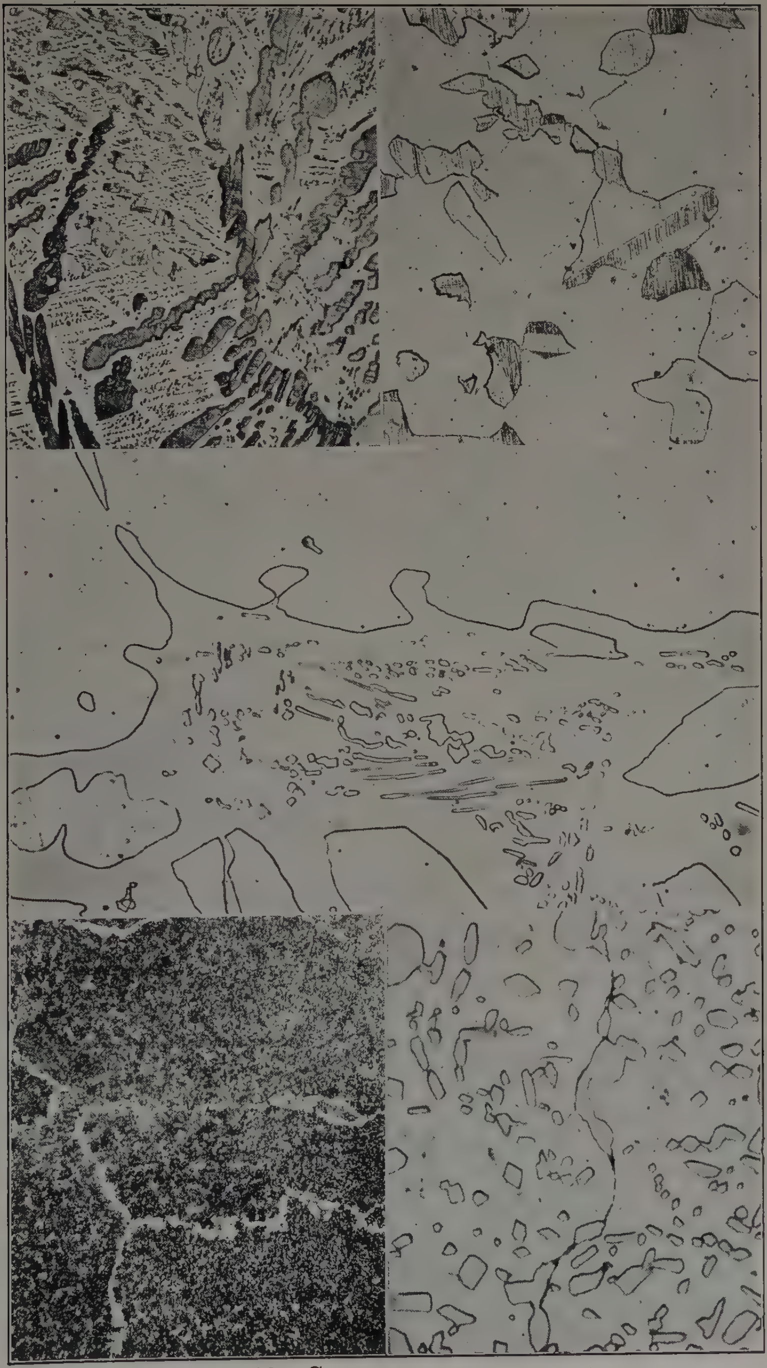
[21] Reference of footnote 14.



Figs. 22–26.—Captions on opposite page.

539° C. This is 19° C. higher than in the copper-tin system. It is not very probable that the nickel would lower the temperature domain of gamma in one case and raise it in another; therefore, the excess constituent in this field has been designated as a new phase, theta.

On considering the instability of the gamma phase it seemed very likely that the gamma in low-tin alloys changed to theta over a range of temperature; so a sloping line CM was drawn to indicate the boundary between the alpha + theta and alpha + gamma fields. This boundary intersects the alpha boundary at a temperature slightly lower than do the boundaries of the alpha + beta + gamma field.

The microstructure of these alloys, together with those of the higher nickel alloys, discussed later, indicate that the theta phase might be either the compound Ni_4Sn or Ni_3Sn of the nickel-tin system reported by Voss,[22] or what is more probable, one of these compounds containing copper in solid solution.

Alpha + Delta Prime Field.—The alpha + delta prime field was located between 539° C. and room temperature for alloys containing from 16 to beyond 31 per cent tin. The boundary on the high tin side was not determined. The alloys containing from 16 to 20 per cent tin that were quenched at 500° C. and also those cooled to room temperature contained alpha plus a clear delta prime constituent (Fig. 13).

The alloys from 22 to 29 per cent tin consisted of alpha + eutectoid (alpha + delta prime) (Figs. 18 and 22). These photomicrographs show that the amount of alpha precipitate in the eutectoid increased with the tin content. The 22 and 23 per cent tin alloys had very little alpha in the delta prime and most of it was in the center of the delta prime grains, while the 27 and 29 per cent tin alloys had considerable quantities of alpha in the delta prime phase.

The existence of the new phase delta prime was established by the following observations:

1. On etching with acid ferric chloride, delta prime was white, while the gamma constituent in alloys from 18 to 29 per cent tin varied in color from a pale blue to a dark blue-brown color respectively.
2. The thermal examinations of the alloys from 16 to 29 per cent tin indicated a thermal change at 539° C. which was in agreement with a phase transformation.
3. The difference in the behavior of the delta prime phase from all other phases when examined under polarized light. A large number of alloys were examined under polarized light so that the behavior of every phase in the diagram could be determined. The results show that in every case the delta prime phase reversed colors when rotated in the polarized light. On rotating 360°, it was white twice and dark twice. It did not reverse as a solid mass but as individual crystals. First one would

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[22] Reference of footnote 3.

turn dark and then another, depending upon the orientation of the crystals. All of the other phases in this system did not reverse colors when rotated, but remained dark. This indicated that delta prime does not have a cubic structure and that all the other phases do have.

Delta prime, although having the same color and appearance when examined under the ordinary microscopic procedure as the delta of the copper-tin system, differed from it under polarized light. Delta did not reverse colors. According to Westgren and Phragmen[23] delta has a face-centered cubic lattice with 416 atoms to the unit cell. This is without doubt a very peculiar type of structure. A small amount of nickel was sufficient to change this cubic structure to perhaps a tetragonal or a hexagonal phase. This being the case, delta prime would reverse colors when viewed under polarized light.

In the same manner delta prime was distinguished from the theta phase. The line *CMP* was drawn from 14.5 per cent tin, 749° C., to 15.8 per cent tin, 25° C., because there was a definite moving to the right of the corresponding line in the 3 and 5 per cent nickel systems.

The 31 per cent tin alloy quenched at 500° C. contained delta prime + eutectoid (alpha + delta prime). When it was cooled to room temperature the amount of excess delta prime increased. The same phenomena were observed in the 1 per cent nickel alloys. Since the alpha-phase boundary did not vary from 500° to 25° C., the change must be entirely in the delta prime phase. This would indicate that delta prime was a solid solution whose solubility for copper and nickel increased on cooling below the eutectoid transformation.

After considering the structures of the alloys in this field the question arises as to why the high-tin alloys have a eutectoid structure and the low-tin alloys do not. It can be explained in the following manner:

1. The addition of nickel moves the location of the gamma eutectoid to higher percentages of tin. It is assumed that the delta prime phase boundary is moving also to higher tin percentages but not as rapidly as the eutectoid. As the distance between the eutectoid point and the delta prime phase boundary is decreased, the amount of alpha in the eutectoid is decreased.

2. On cooling below the eutectoid transformation, the solubility of copper and nickel in the delta prime is increased so that part of the alpha in any eutectoid present is absorbed by the delta prime.

3. The diffusion rates of the atoms must be greater in the delta prime phase than in the ordinary delta, so that when an alloy is cooled slowly through the eutectoid inversion the resulting phases come to a state that is nearer to equilibrium. In other words, the copper and nickel atoms migrate at a faster rate to either the already existing alpha boundaries or to coalesce with one another and form coarse alpha particles in the delta

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[23] Westgren and Phragmen: *Ztsch. f. Metallkunde* (1926) **18**, 279–284.

prime than in nickel-free alloys. When the delta prime grains are small and the migration distances are short a clear delta prime will result, and when the delta prime crystals are large a coarse eutectoid will be formed. These two cases are represented by the 20 and 29 per cent tin alloys.

The fact that the rate of cooling plays an important part in the structure obtained can be seen by comparing two 20 per cent nickel alloys, Figs. 13 and 24, that were cooled at two different rates. The first structure was obtained by the annealing and very slow cooling treatment used in determining the equilibrium diagram and the second by reheating and cooling this annealed alloy through 539° C. at the rate of 10° C. per minute. The delta prime of the annealed and very slowly cooled alloy is homogeneous while the other has a eutectoidal structure.

The One Per Cent Nickel Copper-tin System

There was such a decided shift in the location of the eutectoid point, gamma to alpha + delta prime, in the 2 per cent nickel copper-tin system from that of the straight bronze that it seemed wise to locate it at some composition between the two systems. Four alloys were made containing 1 per cent nickel with the tin varying from 27 to 30 per cent and were quenched at temperatures varying from 725° to 500° C. A set of alloys also was slowly cooled to room temperature.

The results obtained from the heat treatments of the four alloys are exactly what one would expect to find on assuming a gradual change from the copper-tin system to the 2 per cent nickel quasibinary system. The eutectoid point was located at 28.5 per cent tin.

The Three and Five Per Cent Nickel Copper-tin Systems

The 3 and 5 per cent nickel copper-tin systems were not developed as extensively as the 2 per cent series has been. The alpha-phase boundary together with the solidus and liquidus above that field were determined. Five additional alloys in each system exceeding the alpha limit and containing as high as 29 per cent tin were quenched at the same standard temperature intervals as were the 2 per cent nickel alloys. While the latter observations did not give enough information to fully establish the systems, they do agree with the results obtained for the previous systems and show the general trend of the phase changes caused by further nickel additions. These systems are shown in Figs. 27 and 28.

Liquidus and Solidus.—The temperature of the liquidus in both the 3 and 5 per cent nickel systems was raised 7° C. for each per cent of nickel compared to the copper-tin system.

The solidus horizontal in the 3 per cent nickel system above the alpha + beta field was located at 799° C., which is the same as the 2 per cent nickel system. With 5 per cent nickel it was at 812° C.

Alpha-phase Boundary.—The solubility of tin in the alpha phase in both the 3 and 5 per cent nickel systems decreased from 12.5 to less than

1.5 per cent tin between 780° and 500° C. The shape of the boundary in the 3 per cent nickel quasibinary is very similar to that of the 2 per cent nickel system. The boundary of the 5 per cent system differs from the other two in that the tin solubility decreased more rapidly between 780° and 700° C. No further change in solubility occurred on cooling below 500° C. in either case.

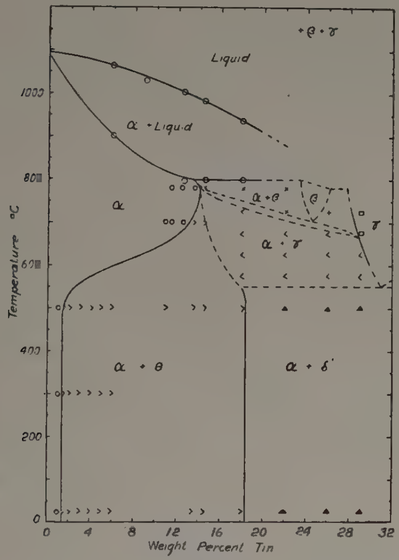

FIG. 27.

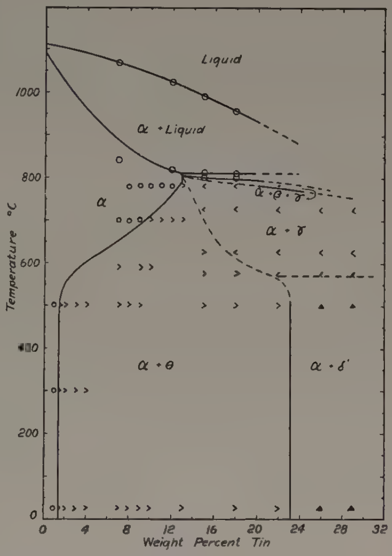

FIG. 28.

FIG. 27.—THE 3 PER CENT NICKEL COPPER-TIN SYSTEM.
FIG. 28.—THE 5 PER CENT NICKEL COPPER-TIN SYSTEM.

Solid Phase Changes Outside Alpha Boundary.—The phases present in the alloys that exceed the alpha boundary show that further nickel additions have a progressive effect on the location of the boundaries of the various fields. As in the 2 per cent nickel system, the addition of 3 and 5 per cent nickel raised the temperature domain and restricted the size of all the areas containing the beta phase. In the 5 per cent nickel system, the alpha + beta + gamma field was within 11° C. of the peritectic horizontal. The rate at which the alpha + beta field has been diminished in size and the raising of the triplex field would indicate that the beta constituent would finally vanish on further nickel additions.

The boundary between the alpha + theta and alpha + delta prime fields was raised to higher percentages of tin in both systems. In the 3 per cent nickel quasibinary the alpha + delta prime alloys containing below 26 per cent tin had a clear delta prime phase, while those above had a eutectoid structure. All of the 5 per cent nickel alpha + delta prime alloys had a clear delta prime phase (Fig. 23). As the nickel was increased from 3 to 5 per cent in the 29 per cent tin alloys the amount of excess alpha increased, indicating that the delta prime phase boundary has been raised to a higher tin content as the nickel increased.

The Ten and Twenty Per Cent Nickel Copper-tin Systems

The study of the 10 and 20 per cent nickel systems has been limited to the determination of the alpha-phase boundary.

The 10 *Per Cent Nickel Copper-tin System.*—The diagram of this system is shown in Fig. 29. The average increase in the liquidus temperature for each per cent of nickel was 6.8° C. The peritectic horizontal was located at 859° C., which is 61° C. higher than in the simple copper-tin system.

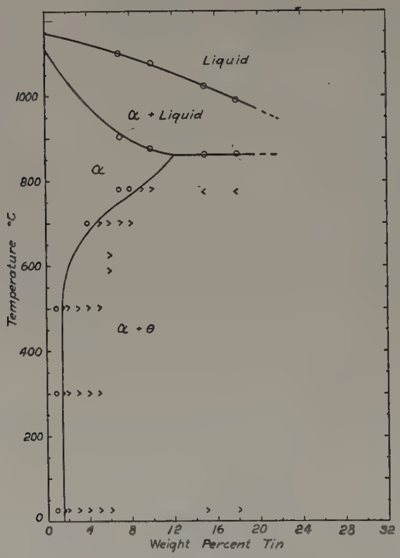

FIG. 29.

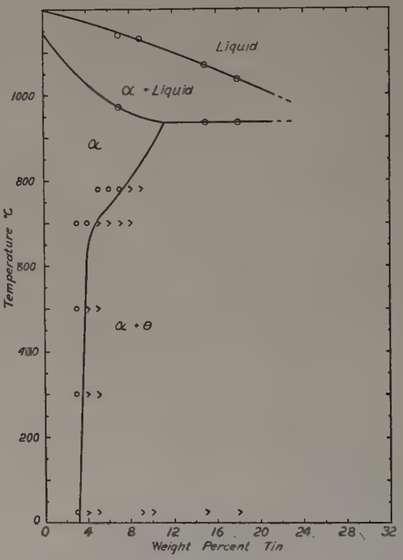

FIG. 30.

FIG. 29.—THE 10 PER CENT NICKEL COPPER-TIN SYSTEM.
FIG. 30.—THE 20 PER CENT NICKEL COPPER-TIN SYSTEM.

The alpha boundary decreased from about 8.7 per cent tin at 780° C. to slightly less than 1.5 per cent at 500° C., and room temperature. The alpha + theta phases were present in alloys exceeding the solubility limit.

The 20 *Per Cent Nickel Copper-tin System.*—The diagram of this system is shown in Fig. 30. The average increase in the liquidus temperature above that of the copper-tin system was 5.7° C. for each per cent of nickel. The peritectic horizontal was located at 936° C., an increase of 138° C.

There was not as great a decrease in the solubility of tin in the alpha with decreasing temperature as in the other systems. This alpha solubility also differed from the others in that it decreased on cooling from

500° to 25° C. The boundary varied from about 7.2 to 3.1 per cent tin between 780° and 25° C.

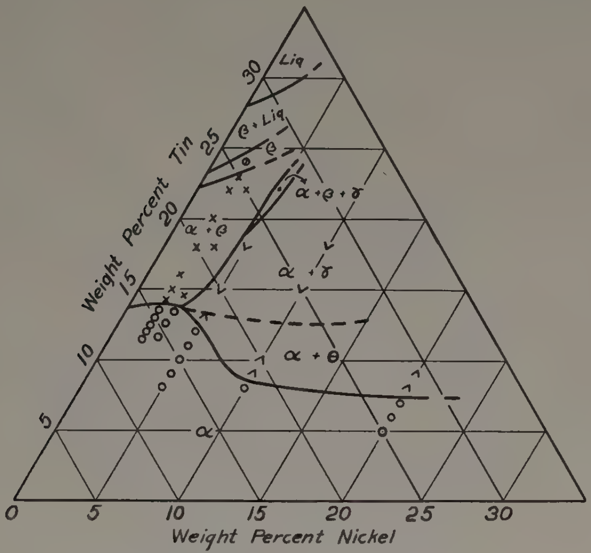

Fig. 31.—The 780° C. isotherm.

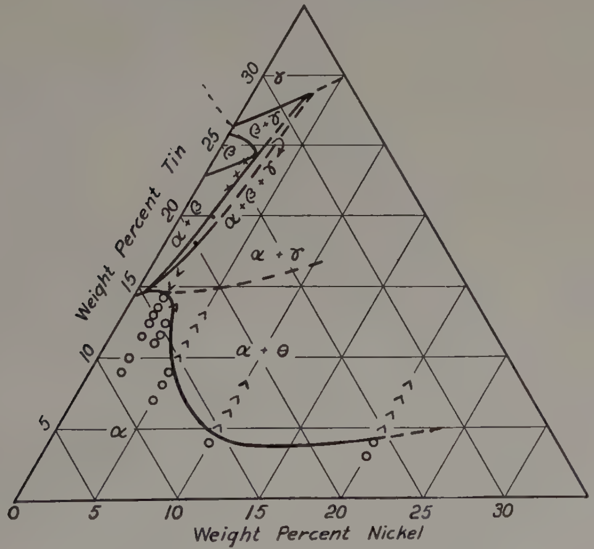

Fig. 32.—The 700° C. isotherm.

Microstructure of Alloys in the Alpha + Theta Field

Upthegrove, Wilson and Rhines[24] found that slowly cooled alloys containing 15 per cent tin and 3 to 10 per cent nickel consisted of dark-etching alpha containing particles of the light theta phase, similar to Fig. 25. Price, Grant and Phillips[25] also found that alloys in the alpha + theta field had a dark color after etching.

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[24] Reference of footnote 5.

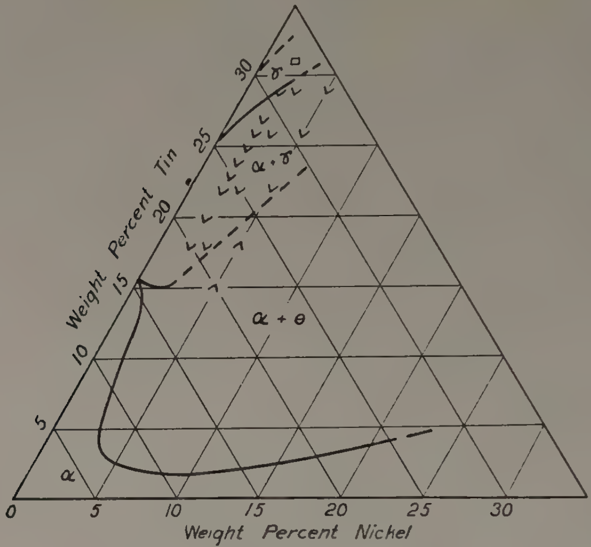

FIG. 33.—THE 575° C. ISOTHERM.

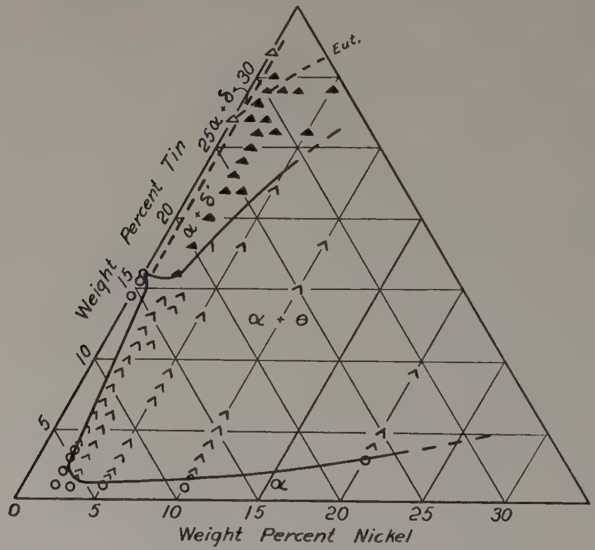

FIG. 34.—THE 500°, 300° AND 25° C. ISOTHERM.

The observations of the present authors show that the microstructure of alloys in this field depends upon the rate of cooling through the temperature range in which the solubility of tin decreases in the alpha phase. When an alloy is cooled fairly rapidly through this temperature range, the theta constituent is precipitated in a very finely divided state in the alpha. After etching, this mixture has a dark appearance as shown in Fig. 25, which is a photomicrograph of a 5 per cent nickel and 13 per cent tin alloy cooled from 700° to 500° C. in 10 hr. When these alloys are cooled at a much slower rate, the theta phase coalesces into large grains and the alpha matrix is clear after etching. Fig. 26 shows the clear alpha matrix and large theta particles in a 20 per cent nickel, 9 per cent tin alloy which was cooled from 725° to 500° C. in 94 hours.

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[25] Reference of footnote 4.

Summary

The results of the investigation can be summarized clearly by considering several isothermal diagrams of the ternary system. Figs. 31 to 34 give the isotherms at 780°, 700°, 575° and 500°, 300°, 25° C. respectively.

A survey of the isotherms shows that as the nickel is increased the boundaries of the beta and gamma fields move to higher tin contents. As the temperature is lowered all the areas containing the beta phase contract to lower nickel contents. The alpha + gamma field likewise diminishes in size at the lower temperatures.

The gamma and alpha + gamma fields present at 575° C. are replaced by the alpha + delta and alpha + delta prime areas in the 500° C. isotherm (Fig. 34). The dotted line extending from 16 to 32 per cent tin at approximately 0.5 per cent nickel indicates that a definite amount of nickel probably is required to produce alpha + delta prime. The broken line across the top of the diagram indicates the shift in the gamma eutectoid inversion to alpha + delta prime to higher percentages of tin as the nickel is increased in amount.

The solubility of tin in the alpha phase in all the isotherms starts to decrease at the nickel content at which the alpha comes in equilibrium with the theta phase, which varies between about 0.5 and 3.5 per cent nickel.

Conclusions

After considering the various quasibinary systems and the ternary isotherms, the following conclusions were reached concerning the copper-rich alloys of the copper-nickel-tin system:

1. The solubility of tin in the alpha phase of the copper-tin system increases between 590° and 500° C. and then remains constant to room temperature.
2. The transformation in the copper-tin system between 15.5 and 25 per cent tin at 590° C., which was observed by Hoyt, Stockdale and others, is due to a change of the beta phase to alpha + gamma.
3. The liquidus of the bronzes containing up to 18 per cent tin is increased 7° C. for each per cent of nickel added up to 5 per cent. Above

that amount of nickel the gradient diminishes to 5.7° C. at 20 per cent nickel.

4. Alloys containing up to 10 per cent nickel exhibit a greater temperature difference between the liquidus and the solidus horizontal above the alpha + beta field than do the simple copper-tin alloys.

5. The addition of nickel to copper-tin alloys causes the solubility of tin in the alpha phase to increase on cooling below the solidus when the alpha is in equilibrium with the beta phase. The solubility of tin in the alpha decreases on cooling below the temperature at which beta changes to alpha + gamma. A new phase, theta, is then precipitated.

6. The alpha solubility at 500°, 300° and 25° C. decreases from 16 per cent tin at 0 per cent nickel to a minimum of approximately 1.2 per cent tin at 4 per cent nickel, followed by a gradual increase to slightly over 3 per cent tin at 20 per cent nickel.

7. The lattice parameter of the alpha phase of an alloy containing 2 per cent nickel and 12 per cent tin quenched at 780° C. is 3.680 Å. The parameter of the beta phase of an alloy containing 2 per cent nickel and 25 per cent tin quenched at 725° C. is 2.994 Å.

8. The addition of nickel raises the temperature of the beta transformation to alpha + gamma and causes the change to be more sluggish and to extend over a range of temperature. This transformation does not occur at constant temperature, but takes place at higher temperatures as the copper or nickel content increases.

9. The addition of nickel to the delta phase of the copper-tin system causes it to change from a cubic structure to an anisometric structure, which has been designated as delta prime. Delta prime is a solid solution in which the solubility of copper and nickel increases on cooling below the eutectoid transformation; thus causing an absorption of part of the alpha.

10. The addition of nickel causes the gamma eutectoid point to move to higher tin contents.

11. In alloys containing 2 per cent nickel and at least 16 per cent tin, the gamma phase changes to alpha + delta prime on cooling through 539° C. Whether or not the eutectoid structure of alpha + delta prime is obtained, depends upon the rate of cooling. A rapid rate of cooling tends to give a fine eutectoid structure, while a very slow rate of cooling gives a clear delta prime phase in the low-tin alloys and a coarse eutectoid structure in the high-tin alloys. By slow cooling the alpha is given an opportunity to coalesce at the grain boundaries.

12. Alloys in the alpha + theta field containing at least 5 per cent nickel when cooled to room temperature may contain either a clear or dark-etching alpha matrix, depending upon the rate of cooling through the temperature range in which the solubility of tin in the alpha phase decreases. A relatively fast rate of cooling causes the theta constituent to separate in a very fine precipitate in the alpha, causing a dark

appearance on etching. A very slow rate of cooling allows the theta phase to coalesce to large grains and the alpha remains light in color.

ACKNOWLEDGMENTS

The authors desire to express their appreciation to Prof. W. P. Wood and to Prof. Lars Thomassen for their cooperation and assistance in this investigation; and to Messrs. O. Leone, D. McCutcheon, and J. Lester, who aided in the experimental work.

DISCUSSION

(*Robert F. Mehl presiding*)

O. A. CARSON, Kingston, Ont., Canada (written discussion).—I am unable to agree with the copper-tin diagram derived by the authors, particularly the beta and gamma fields. This section has been one of the chief sources of controversy in regard to the copper-tin alloys since Hoyt located the horizontal at 590° C. between 15 and 25 per cent tin. Alloys containing 26.5 per cent tin quenched at 640° C. and at 540° C. all gave identical body-centered cubic patterns when examined with X-rays.[26] It appears to be generally conceded that beta is body-centered cubic and therefore it seems reasonably certain that both alloys were beta. Further, the microscope fails to reveal any structural change in alloys containing 20 to 26.5 per cent tin on passing the 590 horizontal, which would indicate a change from beta to gamma.

I would also like to point out that the results obtained by the authors on the 27 per cent tin alloy appears to be in excellent agreement with those given in my paper for this alloy. This can be seen readily by examination of the tabulated data[27] on the beta boundary; alloy 15Q, 27 per cent tin, quenched 723° C., consisted of uniform beta while the 27.5 per cent tin quenched at 723° C. consisted of beta plus gamma. At the lower temperature used by the authors, 572° C., both the 27 and 27.5 per cent alloys would lie in the beta field. Therefore the authors' statement on page 229, second paragraph, that "the Carson diagram would require that the alloy (27 per cent tin) quenched at 725° C. be beta + gamma" is not strictly accurate. It must be admitted that the diagram given in my paper might easily lead to this mistake, as the boundary may have been drawn a few tenths of one per cent low at this point and a plot of the 27 per cent alloy would place it at the boundary of beta/beta plus gamma fields. From the description given by the authors of their 27 per cent tin alloys I believe that both consisted of uniform beta and were identical with similar alloys examined in my work. It was undoubtedly due to the large number of alloys to be examined that the 27 per cent tin alloy appears to have been the only composition used to decide this section of the copper-tin diagram, and this was, perhaps, an unfortunate choice. It was very gratifying, however, to find that their results were in agreement with mine in the region of the delta field.

W. B. PRICE, Waterbury, Conn. (written discussion).—On page 224, the statement is made, "Wise found that, owing to the decrease in solubility between high and low temperatures, it was possible to age-harden alloys having compositions within this range." In the paper by Price, Grant and Phillips,[28] considerable space was devoted to the age-hardening of copper-nickel-tin alloys. An alloy consisting of 64.4 per cent copper, 27.6 per cent nickel and 8 per cent tin was specifically described and the Brinell hardness of this chill-cast alloy was increased[29] from 114 to 321 after being homogenized for 100 hr. at 800° C. and drawn at 500° C. Wise, in his discussion of our paper, confirmed the fact that copper-nickel-tin alloys could be age-hardened. It is, however, of importance to note that nearly all of the copper-nickel-tin alloys given by Wise as susceptible to age-hardening contained amounts of other elements such as chromium, silicon, manganese and zinc, varying in amounts from 0.2 to 2 per cent. These additions, especially the silicon and chromium, as stated by Wise, increased the strength at the expense of the ductility.[30] The silicon would also tend to increase age-hardening. I therefore, not Wise, was the first to publish the fact that the copper-nickel-tin alloys could be age-hardened, and in the summary of our paper (item 3, page 514) the statement is made that "a wide range of hardenable copper-nickel-tin alloys has been discovered."

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[26] O. A. Carson: The Bronzes, 80. Reprinted from *The Canadian Mining and Metallurgical Bulletin*, January, 1929. Also reference of footnote 29, 154.

[27] O. A. Carson: *Op. cit.*, 30.

[28] Price, Grant and Phillips: Trans. A.I.M.E. (1928) **78,** Inst. Metals Div., 503.

In the authors' discussion of the paper by Price, Grant and Phillips, the following statement is made: "The excess phase was considered to be beta in all cases." This statement is not strictly in accord with the facts, as we did not consider the excess phase to be beta in all cases. On page 509 the following statement substantiates this: "However, it was early found that an alloy of 90:10 copper-nickel base, containing 8.3 per cent tin, showed no beta when quenched from 800° C. but when slowly cooled was completely 'peppered' with a second constituent." Also, on page 511, the following statement is made, "We are not attempting to describe the constituents, for fear of becoming involved in a controversy as to the possible beta-gamma-delta transformations."

I am glad that the present authors have been able by means of polarized light examinations to differentiate the different phases and give them their proper names, theta and delta prime.

D. Stockdale, Cambridge, England (written discussion).—The writer is gratified to find that the authors' work on the copper-tin system corroborates his own, particularly with respect to the general shape and position of the solidus and to the solubility of tin in copper at low temperatures. With regard to the alloys of higher tin content, it was difficult to decide whether there were two phases in the beta and gamma area as shown in Fig. 8 or whether there were three, as found by Raper. Most workers, however, are now agreed that the copper-rich beta phase undergoes some transformation at 590° C. Raper and Stockdale call the new phase beta prime; the others call it gamma. They all probably mean exactly the same thing and it is unfortunate that a doubt about the existence of a third phase in this area should cause such a confused terminology. The same confusion is increased by the use of the word "polymorphic." "Polymorphism" is the power of a chemical compound to crystallize in two or more forms without change in composition. The writer has found that the beta phase changed over at 590° C. to a second phase, but he missed the separation of any alpha; Raper found that the beta phase first changed to a second phase which then threw out alpha (a stepped transformation). The authors now suggest a two-stepped transformation—Raper's mechanism, in fact. The first step in all three cases appears to be an example of polymorphism, provided that term can be applied correctly to a secondary solid solution that can change over to another form without change in composition. The word "polymorphic" could perhaps be justified in 1925. Even then its use was unfortunate, and it is to be hoped that future workers will avoid it when referring to the literature.

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[29] Price, Grant and Phillips: *Op. cit.*, Table 3.

[30] Price, Grant and Phillips: *Op. cit.*, 514 and Table 4.

The authors' quasibinary diagrams have an unfamiliar appearance and are difficult to reconcile with the phase rule. Many of the discrepancies would disappear if it could be shown that the theta and the delta prime solutions are one and the same phase. It is to be regretted that these solutions were not examined by X-rays. It may be found that one of them contains only two of the elements and that the addition of the third alters and distorts the unit cell in a continuous manner. Such an observation would be of great interest.

E. R. Darby, Detroit, Mich.—My first experience with the copper-tin-nickel system was about 1923. When upon investigating the effect of 5 per cent nickel in leaded bronzes, it was discovered that certain chill castings showed a noticeable increase in hardness after a low-temperature anneal. The alloy, containing 10 per cent tin and 10 per cent lead, was annealed for the purpose of relieving stresses incident to casting, and it was entirely through accident that the hardening effect was noticed. Subsequently, experiments developed that with higher lead contents, this hardening was not evident.

Recent work with lead-free alloys leads me to believe that certain compositions of this system may find important use, but at the present, the marked decline in ductility accompanying the increase of strength by aging dangerously approaches brittleness. By additions of other elements, it is possible that strength and toughness in the annealed and quenched state may be so materially increased that the elongation as drawn is greatly improved. The casting characteristics of the copper-tin-nickel alloys are not any too good and work along the lines of prevention of grain envelopes will have to be done.

W. M. Corse, Washington, D. C.—I have not been in close enough touch recently with technical research to discuss the paper from that angle, but I am glad to see such an authentic and concise presentation of technical information on these particular alloys. Need for it was particularly apparent some years ago when I made a survey of the general subject of the addition of nickel to brasses and bronzes, and at that time I aided in preparing a program of research which we hoped would clear up many of the questions that needed answering. The results of the researches of Messrs. Eash and Upthegrove is a long step in the right direction.

A. J. Phillips, Perth Amboy, N. J.—While the authors have mentioned in Table 1 Hansen's paper in *Zeitschrift für Metallkunde*, in their discussion of the copper-nickel-tin system they do not mention it. I believe that Hansen has demonstrated fairly satisfactorily that the solubility of tin in alpha decreases from 500° C. to room temperature. I did some work on this subject just before Hansen's paper was published and found that an alloy of approximately 16 per cent when heat-treated at 500° C. showed alpha only, but the same alloy upon subsequent heat treatment for several hundred hours of 250° C. showed a fine precipitation of second constituent, probably delta. I believe that the reason most investigations have not encountered this decrease in solubility is that their annealing periods have been too short.

D. W. Smith, Pittsburgh, Pa.—The copper-tin constitutional diagram as set forth by Hamasumi and Nishigori[31] is at variance with the one used by the authors. In my work on segregate structures in copper-tin and silver-zinc alloys,[32] I had occasion to use a copper-tin alloy containing 25 per cent tin which at 550° C. contained alpha and beta phases (proved by X-ray analysis), and not alpha and gamma as the authors' diagram shows, for this concentration and temperature.

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[31] Tohoku Imp. Univ. *Tech. Repts.* (1931) **10**, 131.

[32] Page 48, this volume.

L. L. Wyman, Schenectady, N. Y.—The authors designate Fig. 21 as striated beta phase. On the basis of the photograph shown, the markings are obviously polishing scratches, especially inasmuch as they continue through several fields in parallel lines. The authors, furthermore, do not call attention to similar markings in, for instance, Figs. 18 and 23. I believe that when striations in grains are to be used as proof of a given phase, it would be well to follow the example of Mr. Sykes, who, in his paper on cobalt-tungsten, incorporated sufficient grains to prove undeniably the markings to be striations, and to vary in direction from grain to grain.

R. F. Mehl, Pittsburgh, Pa.—Fig. 9 calls for extensive precipitation from the terminal solid solution. May I ask whether the authors have found or prepared any Widmanstätten or segregate structures in this composition range?

J. T. Eash and C. Upthegrove (written discussion).—The authors appreciate Dr. Carson's comments but do not feel that their data on the 27 per cent tin alloy agrees with the view that on quenching at 725° and 572° C. the alloy would be beta. Their conceptions that the 27 per cent tin alloy would be gamma and that a change occurs at 590° C. in alloys containing between 16 and 25 per cent tin is confirmed by the very definite change in microstructure occurring in these alloys when they carry as little as 0.5 per cent nickel. Numerous observations on alloys in this range carrying 2, 1 and 0.5 per cent nickel point to the beta to gamma change.

The 27 tin, 73 copper alloy quenched at 725° C. lies very close to the boundary of the beta and beta + gamma fields. The copper-tin diagram presented by Dr. Carson shows that this alloy should be beta + gamma. As Dr. Carson states, there must be a slight discrepancy between his data and his diagram.

The authors do not wish to place any misinterpretation on the work of Price, Grant, and Phillips. However, the table of Price, Grant and Phillips giving the constituents of the alloys of binary systems containing varying amounts of tin very definitely lists the excess constituent as beta in all cases. Perhaps this table should have been modified in view of the statement quoted by Mr. Price.

Mr. Price, in discussing Wise's work, apparently has in mind the compositions indicated in the latter's Table 4, which, however, relates solely to the tensile properties of annealed and unaged alloys, and in consequence is not complicated by the factors suggested by Price. Incidentally, it may be noted that these results were, for the most part, based upon tests made in 1921. Wise, in his determination of the solubility relationship of the copper-nickel-tin alloys and in his study of the precipitation hardening of the copper-nickel-tin alloys, used samples of high purity, deoxidized with a small amount of manganese or magnesium, so that no significant errors arose from these impurities. As a matter of fact, Wise, in his discussion of the Price, Grant and Phillips paper, specifically states that alloys containing silicon or phosphorous plus nickel, age-harden, and he was therefore fully cognizant of the complications that might arise in connection with the age-hardening of the modified copper-nickel-tin alloys.

Perhaps, as Dr. Stockdale says, the authors have been guilty of adding to the confusion of terminology used to describe the existence of the various phases, but at the present time they see no reason for preferring beta prime over gamma.

The authors appreciate the comments made by Mr. Darby, as they are particularly interesting from a practical viewpoint.

A study of the casting properties of copper-nickel-tin alloys has been in progress for some time and has resulted in the development of methods for melting and deoxidation, with the result that it is now possible to produce consistently tensile bars which, after suitable heat treatment, develop the following average properties: tensile strength, 96,000 lb. per sq. in.; proportional limit, 55,000 lb. per sq. in.; elongation in 2 in., 10 per cent, and reduction of area 15 per cent.

In view of these results we feel that the casting difficulties mentioned by Mr. Darby have been satisfactorily overcome.

The authors wish to thank Dr. Smith for directing attention to the diagram of Hamasumi and Nishigori; however, the fact that the latter used only one hour as the time of heating leaves the conclusions somewhat questionable.

The striated appearance of the beta phase is quite common. It has also been observed by Stockdale and Carson in their studies on the copper-tin system. Mr. Wyman is right in stating that an area showing a large number of grains should be shown in order to prove that a certain phase has a striated appearance. Fig. 19 shows a large number of beta grains and a close examination will show that the dark grains are striated and that the directions of the striations change with the grains. Unfortunately, the reproduction of this photomicrograph does not show the striations in the light colored beta grains as did the original picture.

We have not intentionally prepared any Widmanstätten structures. However, there is a possibility that some of the alloys in the composition range mentioned by Dr. Mehl do exhibit such structures.

Occurrence of Irregularities in Lead Cable Sheathing and Their Relation to Failures

By W. H. Bassett, Jr.* and C. J. Snyder,† Hastings-on-Hudson, N. Y.

(New York Meeting, February, 1933)

Cable sheaths made from common lead have been used to protect underground cables since the beginning of the power-cable industry. Only within the last few years, however, has a systematic study of the production methods and of the causes of failures in cable sheathing been undertaken. Recent increases in the use and demands for service made upon power cables have emphasized the importance of high-quality cable sheaths. It was customary for the users to attribute the cause for their sheath failures to the lack of purity of the lead, but this contention has not been borne out by field and laboratory inspection of the sheaths.

During the past two years the writers have had an opportunity to examine various types of sheaths that were removed from power cables after failure. These samples were obtained from various parts of the country and represent, it is supposed, the production of the principal cable manufacturers. Aside from corrosion, the common field difficulties can be classified either as mechanical or structural, as outlined below, and when structural irregularities are found they can all be attributed to manufacturing causes and in no way reflect the purity of the lead.

Classification of Cable Sheath Failures Other Than Corrosive

MECHANICAL IRREGULARITIES

A. Splits caused by excessive internal pressure
B. Injuries such as nail holes, cuts, tears, etc.
C. Intercrystalline cracks caused by vibration

STRUCTURAL IRREGULARITIES

A. Splits
  a. Caused by imperfect welds
B. Holes through sheath
  a. Caused by yellow oxide inclusions in sheath wall
  b. Blowouts by entrapped gases during manufacture
  c. Caused by inclusions of dirt and other foreign substances
C. Voids in wall of sheath
  a. Blisters
  b. Laminations
D. Questionable structures
  a. Prominent flow lines
  b. Large areas filled with suboxide
  c. Scattered yellow oxide or dirt

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* Technical Superintendent and Metallurgist, Anaconda Wire & Cable Co.
† Assistant Metallurgist, Anaconda Wire & Cable Co.

After studying such field samples the authors manipulated the operation of lead presses for extruding cable sheathing in such a way as to reproduce experimentally the structural irregularities found in the field samples, thus establishing the cause and supplying operating data for preventing or minimizing their occurrence in regular production.

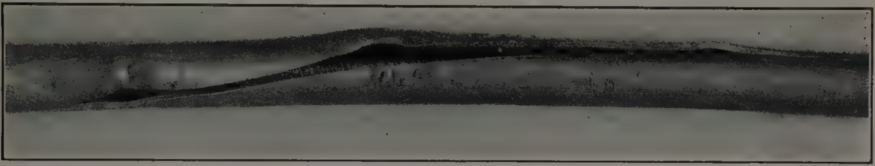


FIG. 1.—SPLIT CABLE SHEATH FROM FIELD.

ILR brand, common desilverized lead, and St. Joe brand, chemical lead, were used for experiments. The ingots were melted in oil-fired kettles of 19,000 and 5000 lb. capacity, which is at least eight times that of the lead press container. Watson Stillman 3000-ton and 1500-ton presses were used. In the larger press the water cylinder is 36 in. in diameter and the ram 12 in. The latter is used to force the lead from the

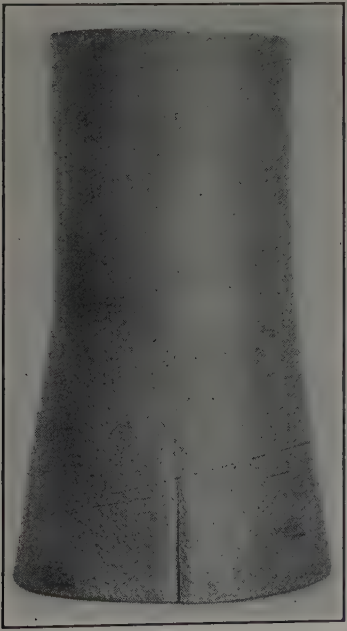


FIG. 2.

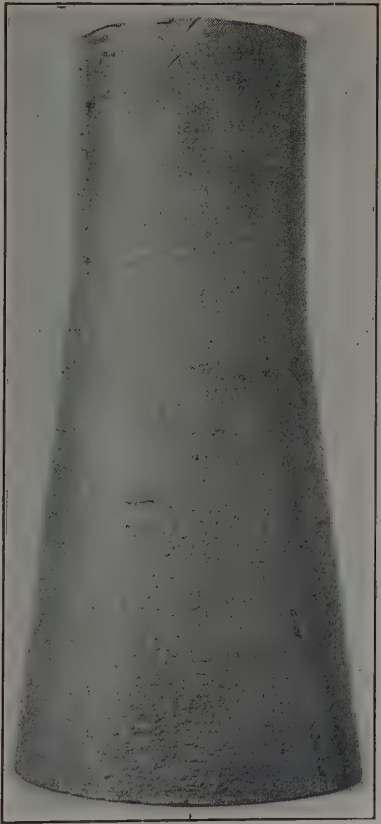


FIG. 3.

FIG. 2.—EXPERIMENTAL SHEATH WITH DEFECTIVE WELD EXPANDED 30 PER CENT.
FIG. 3.—EXPERIMENTAL SHEATH WITH STRONG WELDS EXPANDED 47 PER CENT.

lead container (12 in. dia. by 42 in. deep) into a Watson Stillman die block. This block contains a bridge which separates the lead stream and causes it to flow around the core (9 in. in diameter). When filled, the die block holds a 110-lb. slug. At times a Western Electric type of bridgeless block, which eliminates the top die weld in a sheath, was used with this press. In the smaller press the diameter of the water cylinder is 24 in. and of the ram 8 in. The lead is forced from the lead container (8 in. dia. by 18 in. deep) through a Robertson die block using a core $4\frac{15}{16}$ in. in diameter. This block also has a bridge above the core. When filled with lead this block holds a 60-lb. slug.

In Fig. 1 is shown a typical split sheath which was removed in the field during installation of the cable. In Fig. 2 is shown an experimental sheath made to duplicate the field trouble. In this case the lead container was charged with the lead at 650° F. Similar results were obtained by using an excessive amount of lubrication on the walls of the container on the lead press, and on the lead ram. Fig. 3 shows an experimental sheath produced when the lead temperature was 750° F.

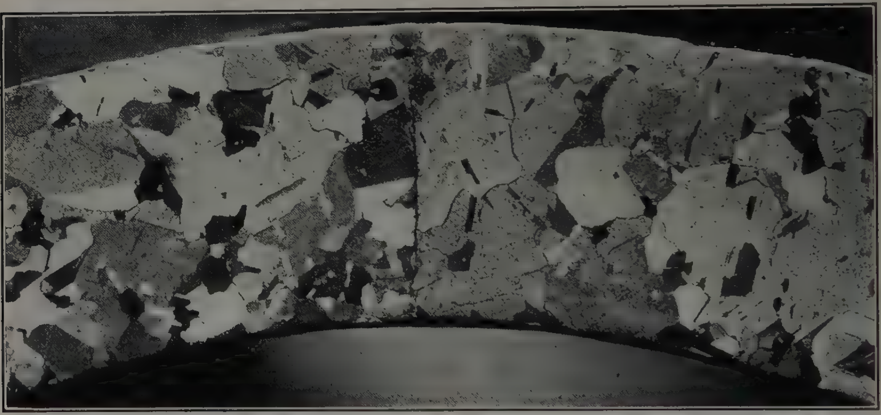


FIG. 4.—POOR TOP WELD IN SHEATH SHOWN IN FIG. 1. × 15.

Microscopic examination of the welds in these three samples clearly revealed that the lead in the field sample had not united at the top longitudinal or radial weld (Fig. 4). The structure of the defective experimental sample shows a similar thick irregular weld line at the bottom where the split occurred (Fig. 5). In contrast with these appear the sharp top weld and well knitted bottom weld of the good experimental sample (Fig. 6). Repeated tests on the lead presses show that these thick weld lines which result in split sheath can be avoided by maintaining the proper temperature in the melting kettle and die block during the extruding operations.

Figs. 7 to 16 inclusive show various other troubles found in the sheaths removed from failed cables. The microscopic examination of these samples reveals clearly the reasons for their existence. In the case

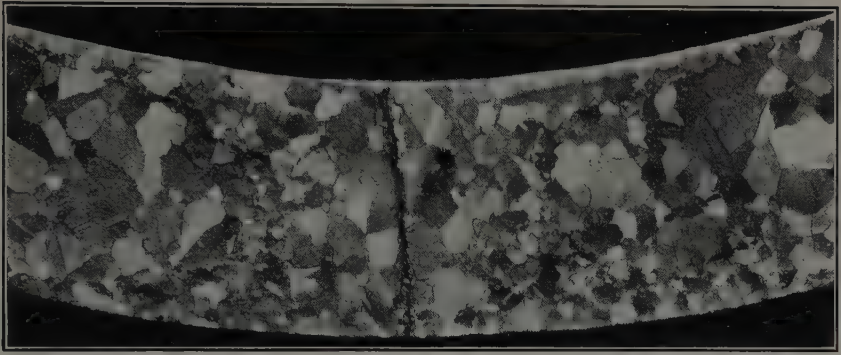


FIG 5.—POOR BOTTOM WELD IN SHEATH SHOWN IN FIG. 2. × 10.

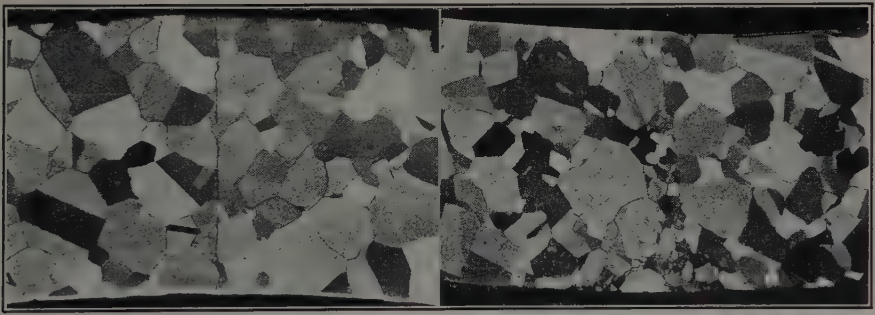


FIG. 6.—TOP AND BOTTOM WELDS IN SHEATH SHOWN IN FIG. 3. × 10.

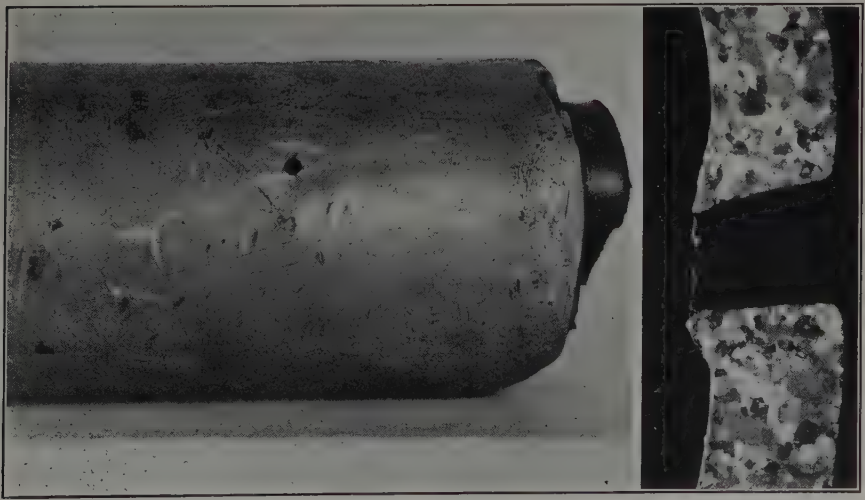


FIG. 7.—NAIL HOLE THROUGH CABLE SHEATH.

shown in Fig. 7, the cable was injured by a nail and the sectional view shows how the contour of the sheath has been disturbed by the force of the penetrating nail. Fig. 8 shows a large lump of yellow and red oxide embedded in the lead. Fig. 9 shows a seam filled with yellow oxide, on the inside surface of a cable sheath, and at one end of the seam the hole resulting from failure of the cable. These yellow oxide inclusions are nonmetallic in nature, lacking strength, ductility and adhesion to the surrounding metal. They dissolve readily, leaving voids when etching the lead for grain structure.

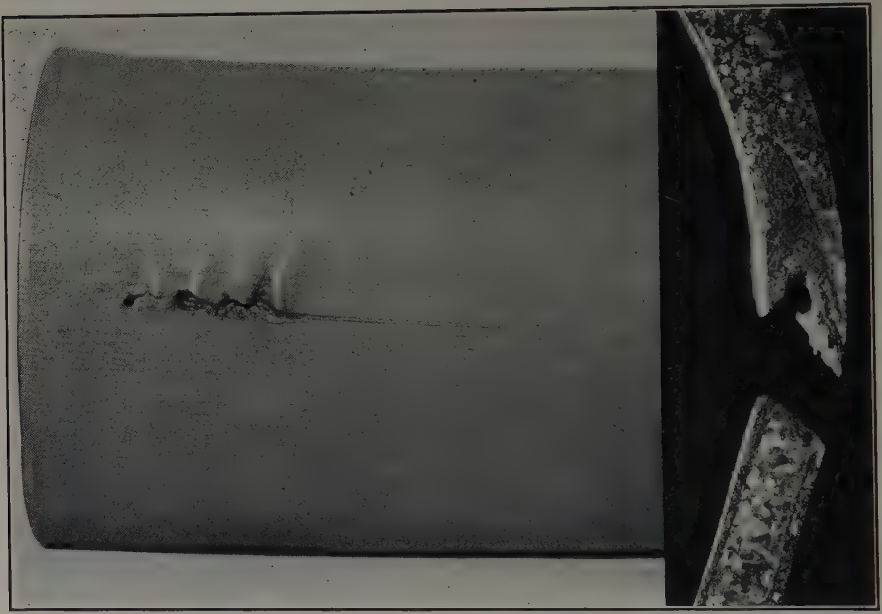


Fig. 8.—Large yellow oxide inclusion in lead sheath with section through inclusion etched for structure.

Fig. 10 illustrates a small blowout during manufacture and shows how the metal has been forced outward by the entrapped gas. In Fig. 11, a case is shown in which the arc from the cable failure has destroyed the direct evidence, if any existed, of the cause of the failure. A micro-examination of the adjacent sheath, however, disclosed entrapped dirt, the dark raised particles shown in Fig. 12, which were probably responsible for a hole in the sheath. Fig. 13 shows a typical blister in a sheath. Blisters are usually caused by the presence in the lead of dirt and other foreign substances which prevent coalescence of various portions of the metal when molten. In Fig. 14 is shown the grain structure surrounding an experimentally produced blister made by adding floor sweepings to the lead container while filling the press. Fig. 15 shows an attempt by the user to repair with solder a hole left by the removal of a yellow oxide inclusion. The solder is readily identified as the gray mass at the top of the picture. As shown, soldering of defects is unsatisfactory because the cavities are seldom filled and failure of the cable finally results. If the cable is to be repaired, it is recommended that excessive solder be used so that the entire defect and the adjacent sheath can be covered with a wipe. The appearance of a cable sheath that failed from mechanical vibration and a photomicrograph of a cross-section appear in Fig. 16.

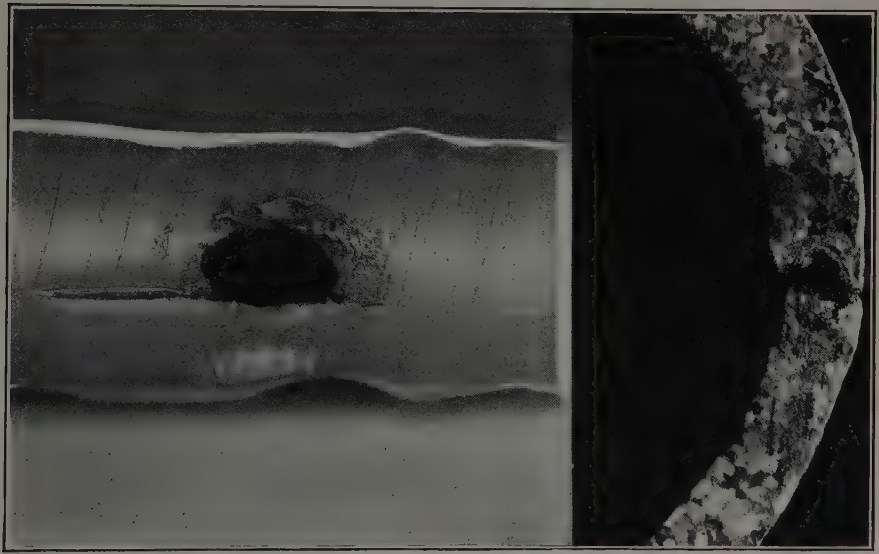


Fig. 9.—Yellow oxide seam and the hole resulting from cable failure with section through seam etched for structure.

When a power cable fails, the arcing of the conductors sometimes destroys the whole sheath at the point of failure, so that the definite cause of the trouble cannot be determined. In these cases, if the lead does not have a uniform appearance at the edge of the "burn-out," or if bending, twisting or other tests show weaknesses in the sheath structure, the report of the user usually states that the lead was not normal and probably contributed to the interruption of the line. Microexamination of the sheath adjacent to such failures often shows an irregular structure, which until recently has been considered questionable, and perhaps falsely blamed because it was not fully understood. Typical examples of these conditions are shown in Figs. 17 and 18. A laminated oxide streak

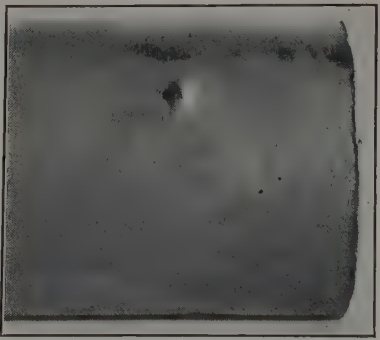


Fig. 10.—Small blowout in cable sheath.

is shown in Fig. 17, which may have caused the cable failure, but the solid oxide streak shown in Fig. 18 was not a fault, as was later definitely proved. A photomicrograph at a magnification of 50 diameters (Fig. 19) clearly illustrates the solidity of this oxide streak. It appears to be made up of flakes of gray suboxide interleaved with metal in such a way as to be both strong and not brittle.

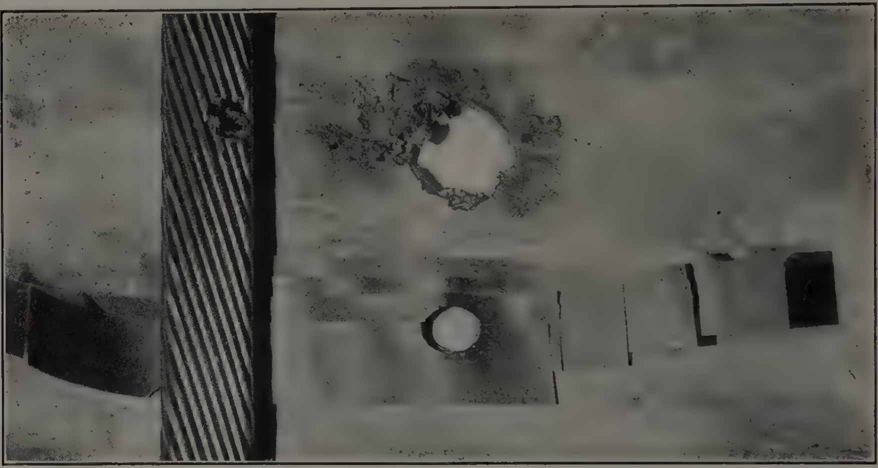


FIG. 11.—HOLE IN CABLE SHEATH AFTER FAILURE OF CABLE.

In order to duplicate these conditions, four complete charges of lead were extruded on both sizes of the lead presses. The lead was heated to 750° F. and transferred to the lead container through an open trough. No attempt was made to prevent it from swirling and splashing as it fell into the lead container. A large amount of foam and dross rose to the top of the molten lead and was allowed to remain as the ram was brought down on the froth, entrapping it in the container. Pressure was applied during the cooling period and then the charge extruded in

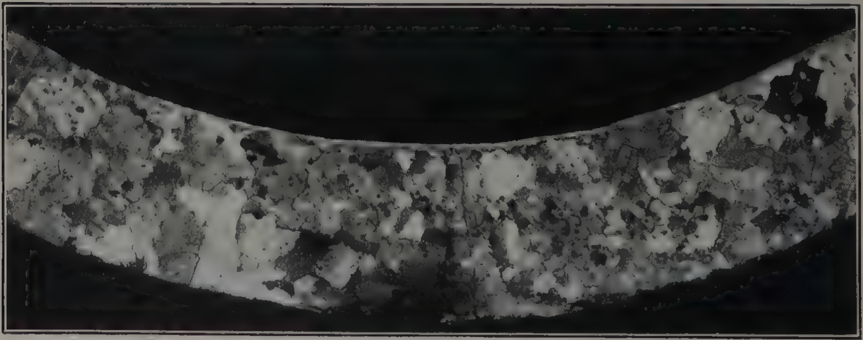


FIG. 12.—DIRT IN STRUCTURE OF LEAD SHEATH. × 10.

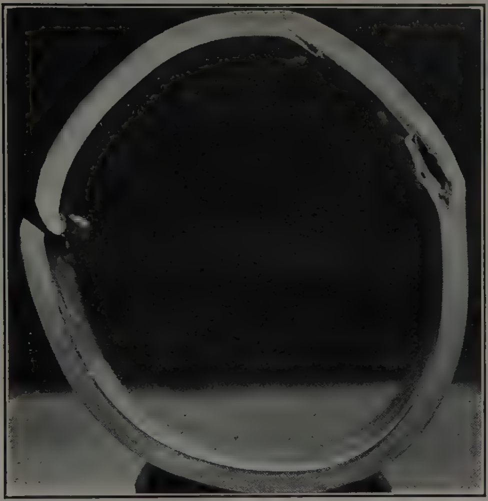


FIG. 13.—BLISTERED CABLE SHEATH.

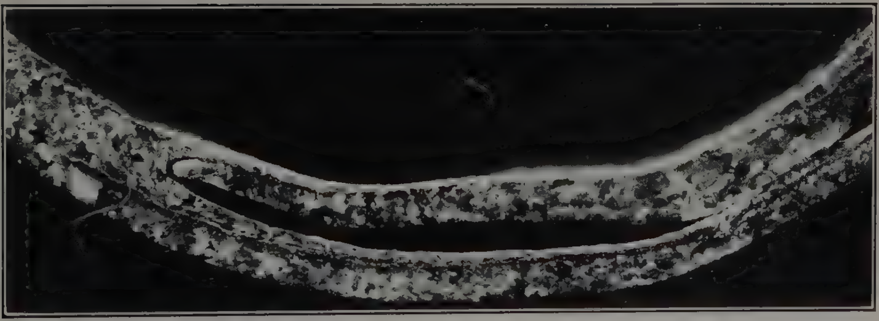


FIG. 14.—STRUCTURE SURROUNDING EXPERIMENTALLY PRODUCED BLISTER. × 5.

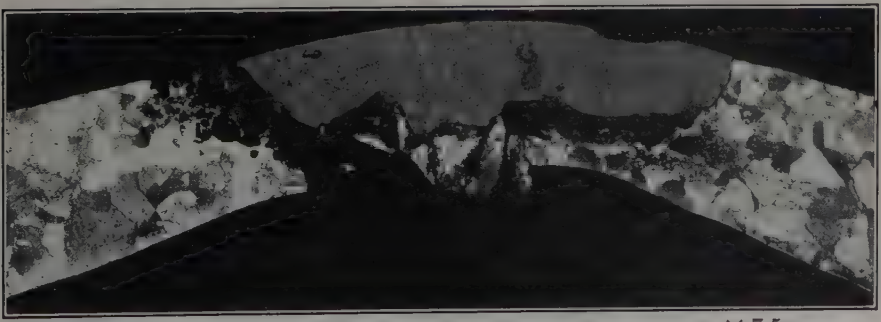


FIG. 15.—DEFECT IN LEAD SHEATH REPAIRED WITH SOLDER. × 7.5.

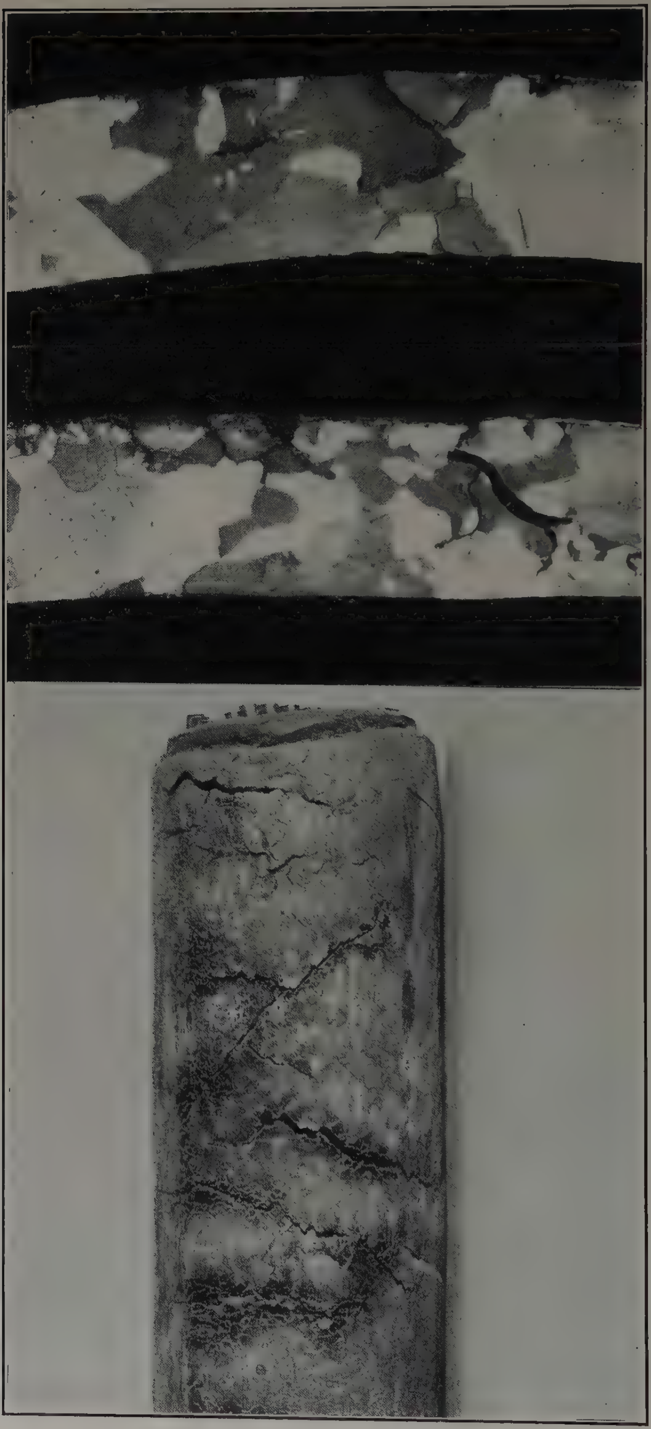


FIG. 16.—INTERCRYSTALLINE VIBRATION-FATIGUE CRACKS IN LEAD CABLE SHEATH.

the regular way, the die block being maintained at a temperature of 400° F. The 2000-lb. extrusions were examined every 7 ft. and the 300-lb. extrusions every 4 ft. throughout their length and in each experiment similar results were obtained. The lead pipe extruded during the first quarter of the stroke of the ram contained the major structural irregularities, while that extruded during the second and third quarters of the stroke was quite uniform in structure, and that extruded during the last

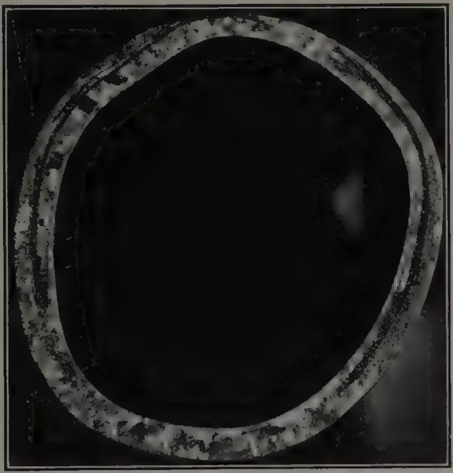


FIG. 17.

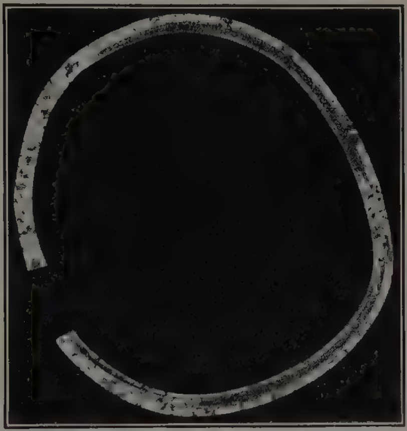


FIG. 18.

FIG. 17.—OXIDE STREAK AND LAMINATIONS IN LEAD SHEATH REMOVED FROM FAILED CABLE.

FIG. 18.—DARK STREAKS IN LEAD CABLE SHEATH.

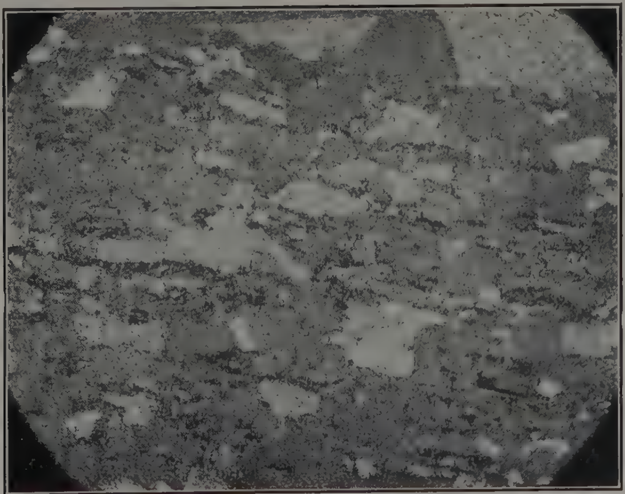
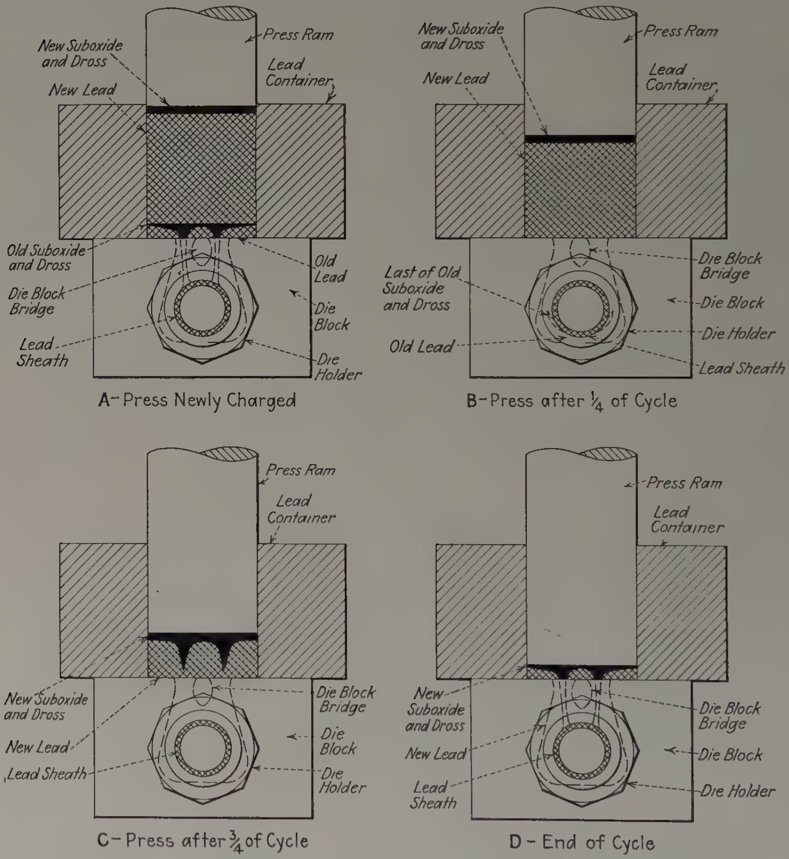


FIG. 19.—STRUCTURE OF OXIDE STREAK IN SHEATH SHOWN IN FIG. 18.

quarter again showed irregularities near the end of the stroke, but not to the extent of the first sheath extruded. The diagrams (Fig. 20) show the probable movement of the dross during the cycle of operations.

The general grain structure of various cross-sections of one of the 2000-lb. charges is shown in Figs. 21 to 29. The sections were cut at points 14, 21, 28, 35, 49, 77, 149, 217 and 238 ft. (the end), respectively, from the start of the extrusion. The new charge of lead first appears in the sheath as an island separated from the old charge by streaks of suboxide which meet at both ends, forming tongue-shaped areas (Fig. 22). As the charge progresses, the new lead works nearer to the top and bottom of the sheath and the amount of oxide diminishes (Figs. 23, 24 and 25). This point marks the extrusion of about one-fifth of the lead charge. The flow lines, which now contain practically no oxide, continue to recede



A- Press Newly Charged

B- Press after ¼ of Cycle

C- Press after ¾ of Cycle

D - End of Cycle

FIG. 20.—PROBABLE MOVEMENT OF LEAD OXIDE AND DROSS AS INDICATED BY FOLLOWING SECTIONS FROM EXTRUSION CYCLE.

in size and prominence until beyond the middle of the cycle they become almost indistinguishable (Figs. 26 and 27). After extrusion of about seven-eighths of the charge, new streaks of suboxide, commonly called "piping," again appear in the structure of the sheath (Figs. 28 and 29). These markings are caused by the center of the charge extruding faster than the outside of the charge, which takes place in certain designs of equipment. Similar piping in the old charge of lead is shown in Fig. 21.

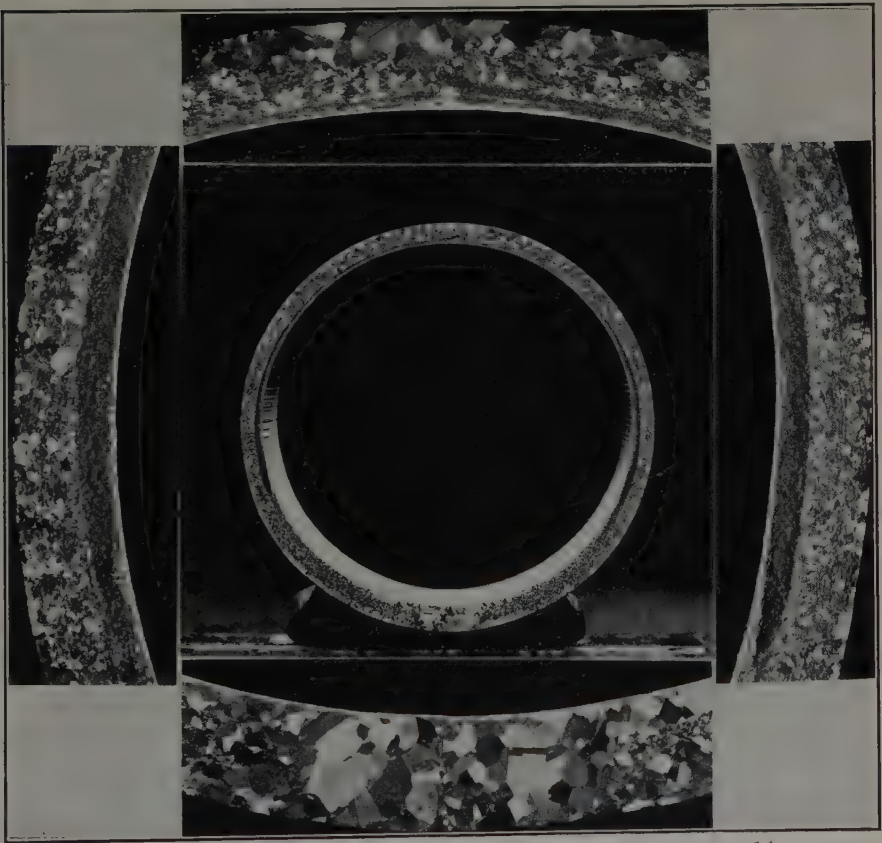


FIG. 21.—STRUCTURE OF SECTION OF CARELESSLY PREPARED LEAD TUBE 14 FT. FROM START OF EXTRUSION CYCLE.

It has been found by experiment that specially designed equipment for handling the molten lead and filling the press container will greatly aid in eliminating oxides and other foreign substances from cable sheathing. Series of pipes were produced under very exacting conditions. The melting kettle was charged only with pigs of lead and was carefully skimmed. All scrap was melted in a separate kettle, cleaned and cast into pigs before using. Further oxidation of the surface was prevented by the use of a reducing agent. The pouring spout at the bottom of the kettle was replaced by a clean pipe 2 in. in diameter, so formed that it directed the molten lead into the lead container with the minimum amount of disturbance and splashing. The container was overfilled and the molten metal skimmed clean. No lubrication was used on the cylinder walls and only a minimum amount applied to the face of the ram. The ram was quickly brought down on the clean surface of the metal and pressure applied during the cooling cycle. The lead was transferred to the press at 750° F. and the die-block temperature was kept at 400° F.

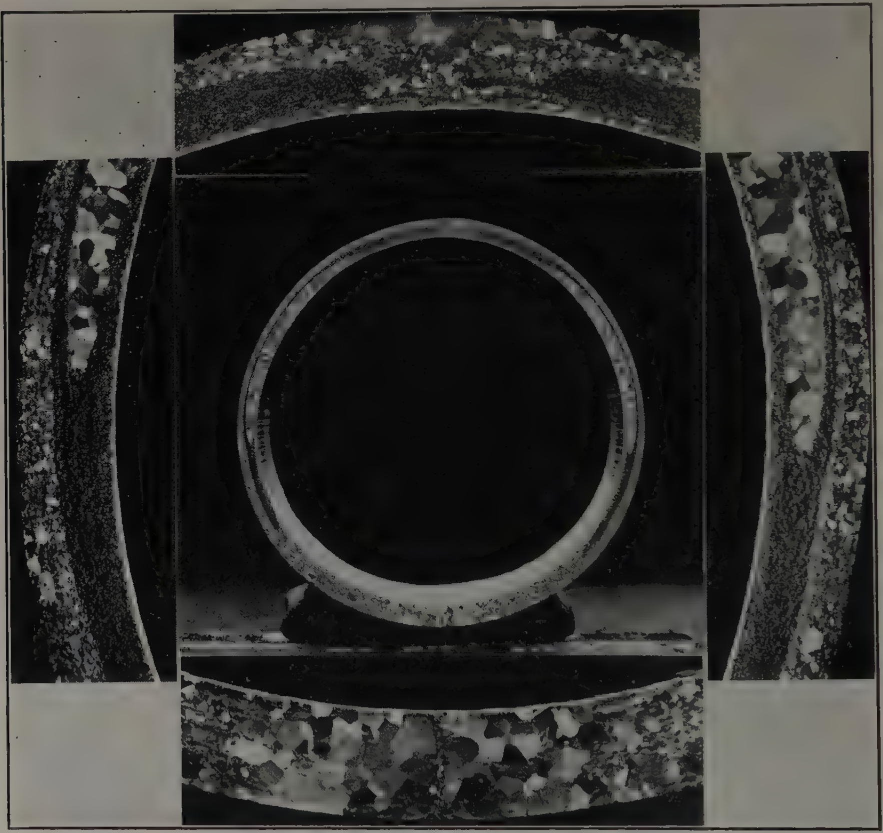


FIG. 22.—STRUCTURE OF SECTION OF CARELESSLY PREPARED LEAD TUBE 21 FT. FROM START OF EXTRUSION CYCLE.

This procedure resulted in a much improved product, containing practically no oxide, as shown in Figs. 30 to 32. These sections represent points corresponding in position to Figs. 22, 23 and 26, respectively. A small amount of oxide can be seen in Fig. 30, whereas an almost perfectly uniform structure is revealed in Figs. 31 and 32.

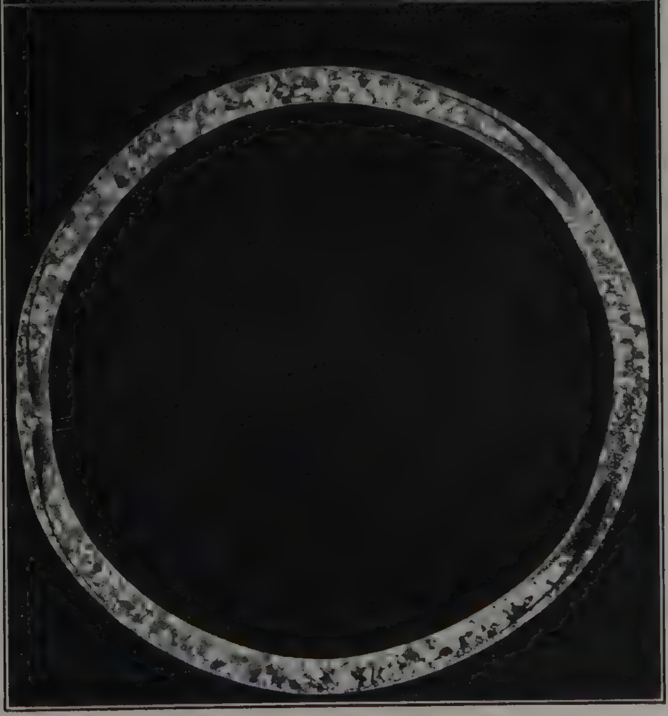


FIG. 23.—STRUCTURE OF SECTION OF CARELESSLY PREPARED LEAD TUBE 28 FT. FROM START OF EXTRUSION CYCLE.

FIG. 24.—STRUCTURE OF SECTION OF CARELESSLY PREPARED LEAD TUBE 35 FT. FROM START OF EXTRUSION CYCLE.

The appearance of all specimens described and illustrated herein is that obtained when the specimens are hand polished and etched in dilute nitric-acetic acid as proposed by the authors.[1]

CONCLUSION

The examination of the field samples and the study of sheath experimentally prepared under controlled conditions leads to several definite conclusions:

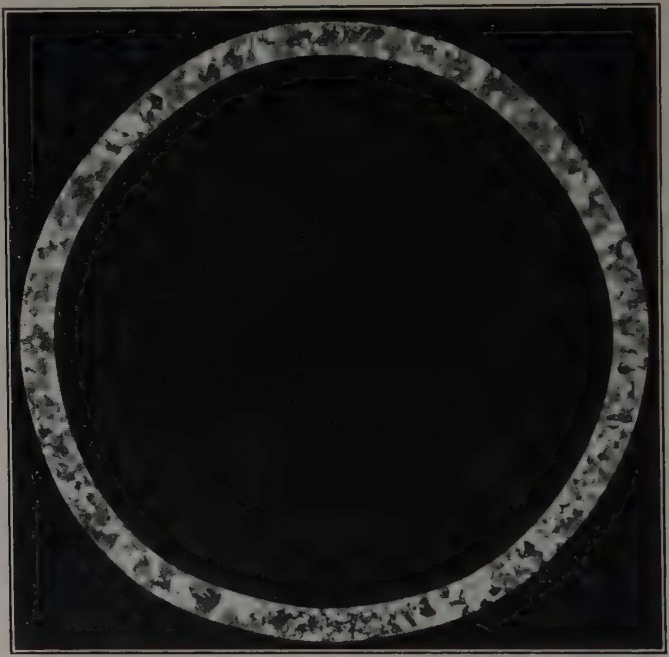


FIG. 25.—STRUCTURE OF SECTION OF CARELESSLY PREPARED LEAD TUBE 49 FT. FROM START OF EXTRUSION CYCLE.

1. That split lead caused by defective welds can be avoided by maintaining the proper extrusion temperature, and by avoiding excessive lubrication of the lead cylinder.
2. That the prominent streaks and large areas filled with suboxide often found in field samples can be avoided by good foundry practice and proper supervision of the melting and extrusion cycles. It is probably not possible in a commercial sense to eliminate all suboxide from the sheath extruded during the first quarter of each extrusion cycle, but that which remains can be reduced to an insignificant amount.

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[1] Methods of Preparation of Lead and Lead Alloy Cable Sheath for Microscopic Examination. Amer. Soc. Test. Mat. (1932) **32,** II, 558.

3. That defects such as blisters, yellow oxide inclusions, dirt, etc., in cable sheath can be entirely eliminated by the separate melting of scrap and by using special pouring equipment when filling the press container.

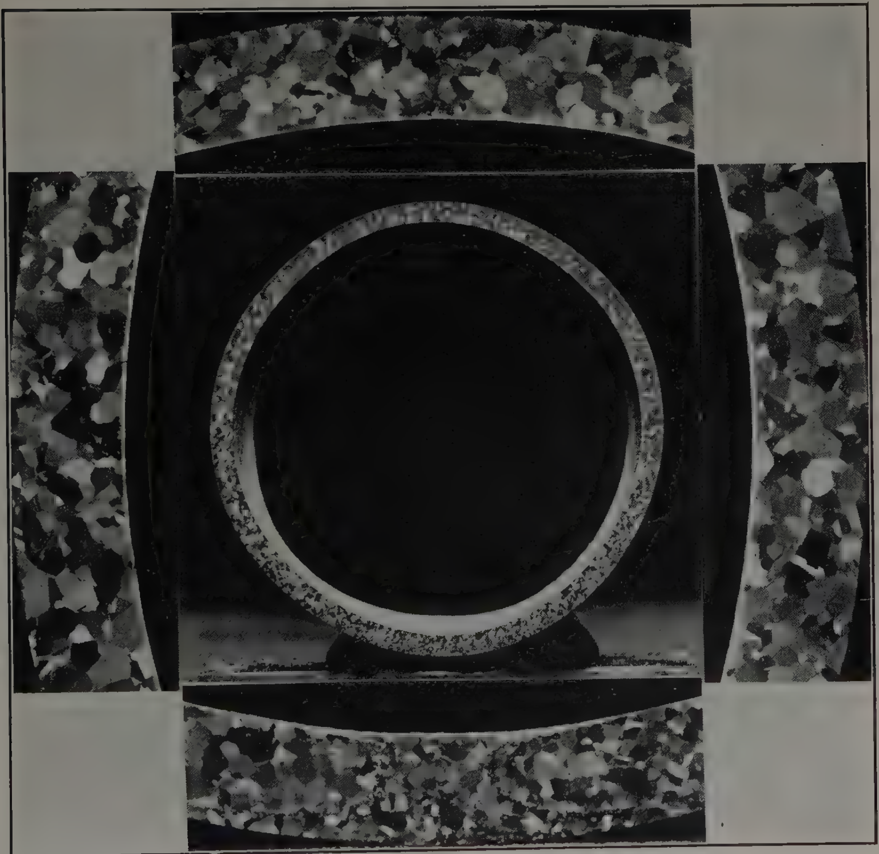

Fig. 26.—Structure of section of carelessly prepared lead tube 77 ft. from start of extrusion cycle.

Bibliography

1. The Theory and Practice of Compression Machines for Making Lead Pipe. *L'Industria* (Nov. 13–Dec. 25, 1904).
2. Sheldon: The Extrusion of Lead Pipe. *Amer. Mach.* (1919) **51,** 909; *idem* (1920) **52,** 59.
3. Archbutt: Failure of the Lead Sheaths of Electric Cables. *Trans.* Faraday Soc (1921) **17.**
4. Dunsheath: The Corrosion of Lead-covered Wiring by Oak. *Elec. Rev.* (1922) **90,** 691.
5. Vilella and Beregekoff: Polishing and Etching Lead, Tin and Some of Their Alloys for Microscopic Examination. *Ind. & Eng. Chem.* (1927) **19,** 1049.

6. Lucas: Application of Microtome Methods to the Preparation of Soft Metals for Microscopic Examination. *Proc.* Inst. of Metals Div., A.I.M.E. (1927) 481.
7. O. Haehnel: Intercrystalline Brittleness of Lead. *Ztsch. f. Metallkunde* (1927) **19,** 492.
8. Hirschfeld, Meyer and Cornnell: Mechanism of Cable Failures. *Elec. World* (1927) **90,** 987.

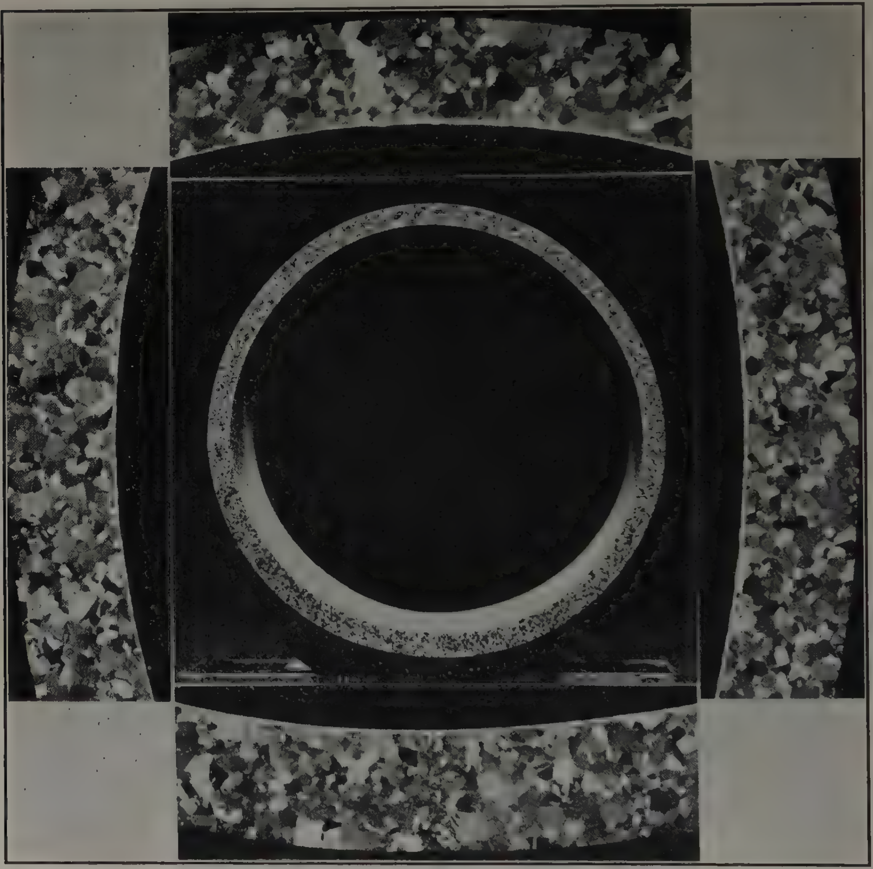

FIG. 27.—STRUCTURE OF SECTION OF CARELESSLY PREPARED LEAD TUBE 149 FT. FROM START OF EXTRUSION CYCLE.

9. Hiers: Characteristics of Very Pure and Commercial Leads. *Trans.* Amer. Inst. Chem. Engrs. (1927) **20,** 131.
10. Burns and Freed: Corrosion of Cable Sheath in Creosoted Wood Conduit. *Jnl.* Amer. Inst. Elec. Engrs. (1928) **47,** 577.
11. Beckinsale and Waterhouse: The Deterioration of Lead Cable Sheathing by Cracking, and Its Prevention. *Jnl.* Inst. of Metals (1928) **39,** 375.
12. Dunsheath and Tunstall: The Physical Properties of Lead Cable Sheaths. *Jnl.* Inst. Elec. Engrs. (1928) **66,** 280.
13. Beaver: The Physical Behavior of Lead Sheaths in Relation to Failures of High Voltage Cables. *Elec. Rev.* (1929) **104,** 96.
14. Wood: High Pressure Cables. *Elec. Rev.* (1929) **104,** 370.

FIG. 28.—STRUCTURE OF SECTION OF CARELESSLY PREPARED LEAD TUBE 217 FT. FROM START OF EXTRUSION CYCLE.

15. Beavis: Water Penetration Effects in Lead Sheathed Power Cables. *Jnl.* Inst. Elec. Engrs. (1930) **68,** 434.
16. Clark and Upthegrove: Flow Characteristics of Some Lead Cable Sheaths at Temperatures Above Normal. Amer. Soc. Mech. Engrs. (June, 1930).
17. Anonymous: The Corrosion of Lead. *Engineering* (British) (1930) **129,** 494.
18. F. Hargreaves: Heat-Treatment, Ball-Hardness and Allotropy of Lead. *Jnl.* Inst. of Metals (1930) **44,** 149.
19. F. Brenthel: Influence of Re-crystallization on the Technical Behavior of Lead. *Ztsch. f. Metallkunde* (1930) **22,** 23.
20. Pearson and Smythe: Influence of Pressure and Temperature on the Extrusion of Metals. *Jnl.* Inst. of Metals (1931) **45,** 345.
21. Allen: Lead Sheaths for Cables. *Elec. Rev.* (1931) **108,** 275 and 321.
22. *Elec. Rev.:* Cable Manufacturing Department. (1931) **109,** 277.
23. O. Haehnel: Crystalline Structure and Embrittlement of Lead. *Elek. Nach.-Tech.* (1931) **8,** 77.

DISCUSSION

(*Albert J. Phillips presiding*)

E. E. SCHUMACHER, New York, N. Y.—Messrs. Bassett and Snyder should be complimented for having obtained such excellent macrographs of ring samples of cable sheath. These show beautifully the relative positions of charge and seam welds. From my own experience, however, I believe that inclusions would have been shown to better advantage had the etching been done in a way to make the lead grains stand out less prominently. Considering the flow of lead in the press, I wonder if the representation given is correct. Usually the lead alloy in the center of the cylinder flows more rapidly than that at the sides. I think the diagram represented the flow through the center and along the sides as being the same.

W. H. Bassett, Jr.—Mr. Schumacher spoke of the other type of etching to bring out the irregularities in the lead. We have studied cable sheaths in this manner, and the reason we did not show any illustrations of that type was that we wanted to bring out the relation of the defect to the crystals in the lead. In Fig. 8 we showed the yellow oxide before the sample had been etched. That had to be done because when the etching solution came in contact with the yellow oxide, it immediately dissolved the material.

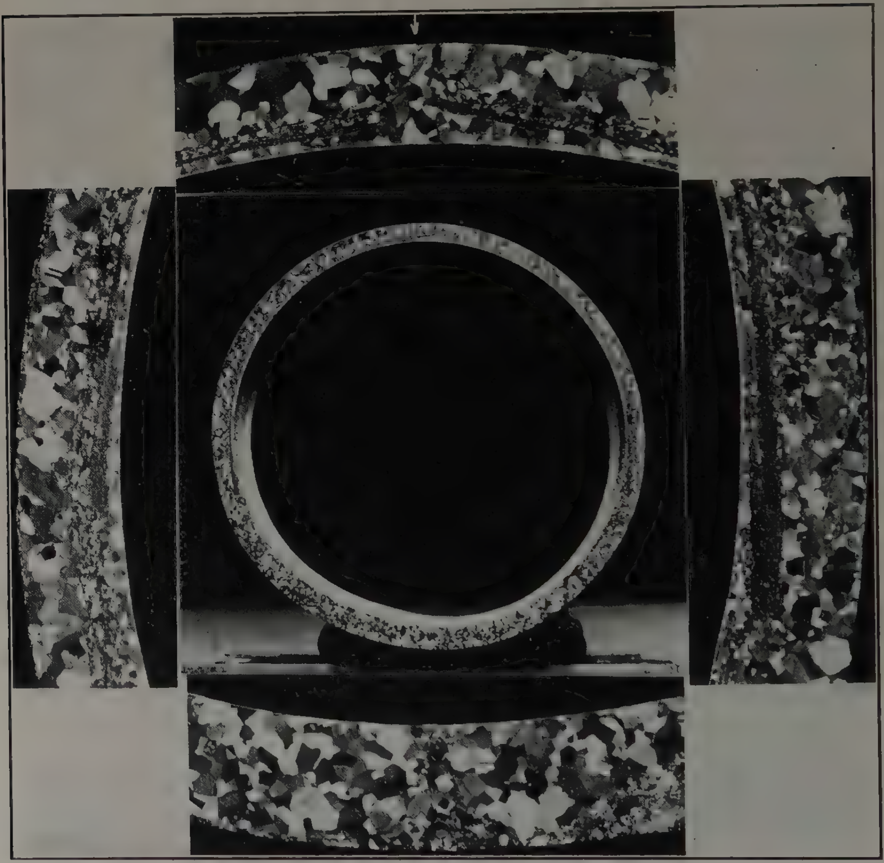

Fig. 29.—Structure of section of carelessly prepared lead tube 238 ft. from start of extrusion cycle (the end).

The diagrams of Fig. 20, showing the flow of lead in the press, were made to illustrate the conditions of the samples that were examined throughout the charge. The lead does flow more rapidly in the center of the lead container, but is divided and somewhat retarded by the bridge. The new charge carrying with it the suboxide forces its way down through the middle of the cavities in each side of the die block. This action is clearly brought out by the islands formed by the new charge, which are surrounded by the old lead, showing that the lead actually does flow more rapidly through the center.

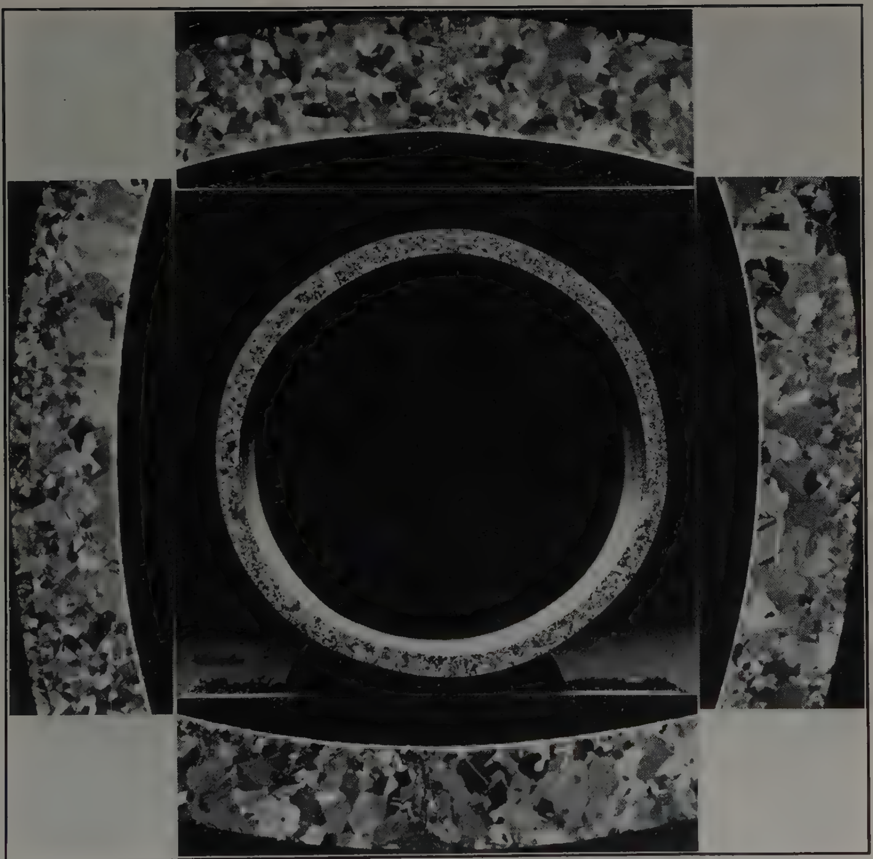

FIG. 30.—STRUCTURE OF SECTION OF CAREFULLY PREPARED LEAD TUBE 21 FT. FROM START OF EXTRUSION CYCLE.

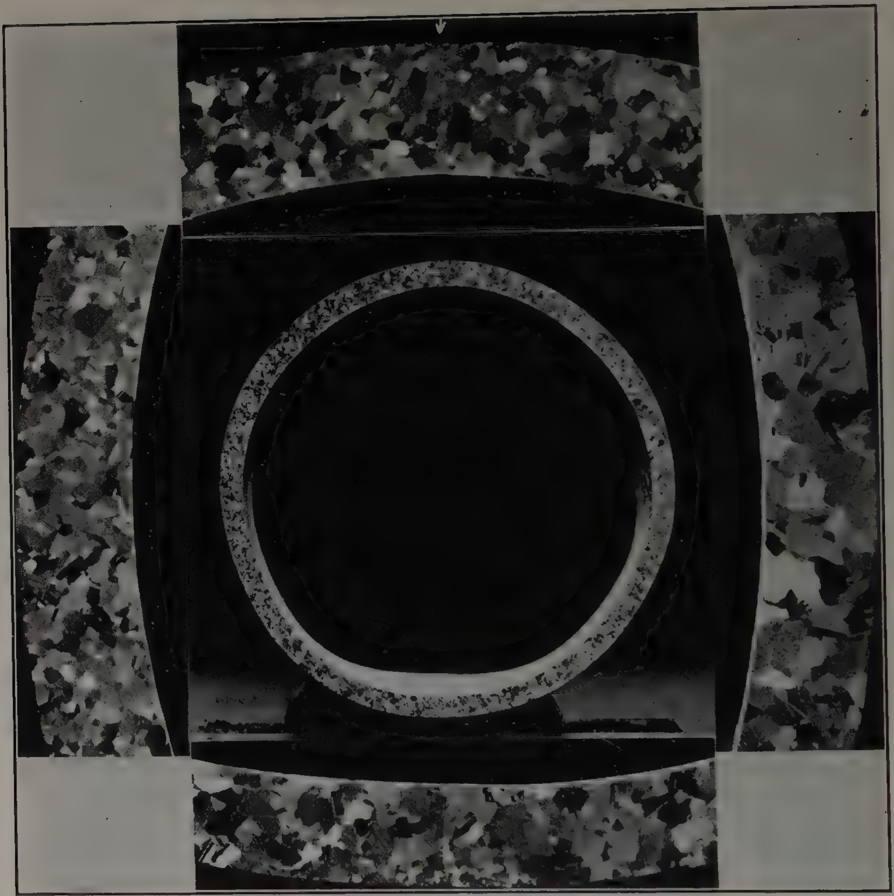

FIG. 31.—STRUCTURE OF SECTION OF CAREFULLY PREPARED LEAD TUBE 28 FT. FROM START OF EXTRUSION CYCLE.

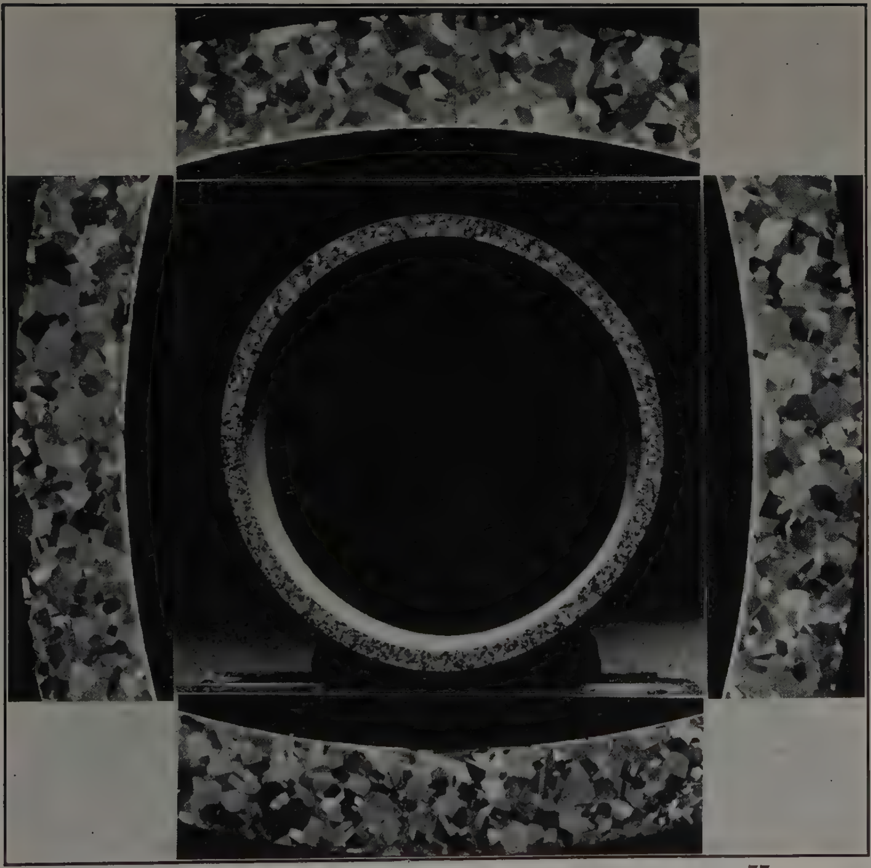

FIG. 32.—STRUCTURE OF SECTION OF CAREFULLY PREPARED LEAD TUBE 77 FT. FROM START OF EXTRUSION CYCLE.

The Role of the Platinum Metals in Dental Alloys, III.—The Influence of Platinum and Palladium and Heat Treatment upon the Microstructure and Constitution of Basic Alloys

By E. M. Wise* and J. T. Eash,† Bayonne, N. J.

(New York Meeting, Febuary, 1933)

In a previous communication[1] the improvement in strength, hardenability and color, occasioned by replacing gold in a typical gold-silver-copper alloy by various amounts of platinum, or palladium, was discussed. In the present paper the results of further studies upon the constitution and the nature of the hardening transformation in these alloys are presented. This research may be summarized as follows:

1. The liquidus and solidus have been determined for the alloys of the palladium and platinum series. Cooling curves were utilized for determining the liquidus of the palladium alloys but this method proved unsuitable for the platinum alloys so that a novel quenching method was utilized for the latter. Both the liquidus and solidus of the palladium alloys increase steadily with the palladium content. The liquidus of the platinum alloys increases rapidly with the platinum content, while the solidus temperature increases with the platinum content up to about 14 atomic per cent platinum, but suffers no further increase with additional increments of platinum up to 20 atomic per cent at least, owing to a peritectic reaction.

2. Palladium, and even more effectively platinum, reduces the rate of grain growth. Owing to this fact and to the increase in the solidus temperature, "overheating" does little or no damage to alloys containing reasonable quantities of these elements. This is confirmed both by tensile tests and metallographic examination.

3. The excess phase present in one of the high-platinum-content alloys has been isolated and chemically analyzed and was found to consist almost wholly of platinum, gold, and copper, evidently derived from the compound AuCu, by the partial replacement of gold by platinum.

4. The variation in the solubility of this platinum-content phase in the alpha solid solution with the temperature has been determined. This

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* Research Metallurgist, The International Nickel Co.

† Metallurgist, The International Nickel Co.

[1] E. M. Wise, W. S. Crowell and J. T. Eash: The Role of the Platinum Metals in Dental Alloys, I and II. *Trans.* A.I.M.E. (1932) **99**, 363.

change in solubility is responsible for the marked age-hardening exhibited by the platinum-containing alloys.

5. The domain of the phases responsible for the hardening of the palladium-content alloys has been determined by dilatometric, X-ray, and metallographic methods.

6. Metallographic studies have been made of the platinum and palladium-content alloys after a variety of heat treatments. The hardened gold and palladium-content alloys exhibit the Widmanstätten type of structure, while the platinum-content alloys usually show a troostitic appearance, although the latter may also be made to develop the Widmanstätten structure by special heat treatments.

TABLE 1.—*Wrought Precious-metal Wires*

Alloy No.	96	97	98	99	100	101	102		103	104	105	106
							ATOMIC PER CENT					
Pd		5	10	15	20	25	30	Pt	5	10	15	20
Au	50	45	40	35	30	25	20	Au	45	40	35	30
Ag	20	20	20	20	20	20	20	Ag	20	20	20	20
Cu	29	29	29	29	29	29	29	Cu	29	29	29	29
Zn	1	1	1	1	1	1	1	Zn	1	1	1	1
							WEIGHT PER CENT					
Pd		4.0	8.2	12.7	17.6	22.9	28.6	Pt	7.0	14.0	21.1	28.1
Au	70.8	65.8	60.6	55.0	49.0	42.3	35.2	Au	63.8	56.7	49.6	42.6
Ag	15.5	16.0	16.6	17.2	17.8	18.5	19.2	Ag	15.5	15.5	15.5	15.5
Cu	13.2	13.7	14.1	14.6	15.1	15.7	16.4	Cu	13.2	13.3	13.3	13.3
Zn	0.5	0.5	0.5	0.5	0.5	0.6	0.6	Zn	0.5	0.5	0.5	0.5

7. X-ray diffraction studies have indicated that the gold and palladium-content alloys quenched from temperatures within the alpha solid solution range previous to aging contain only a face-centered cubic phase. The age-hardening treatment caused the complete conversion of the 50 atomic per cent gold alloy into the face-centered tetragonal form. This phenomenon is similar to the formation of martensite in freshly quenched steel and is unlike the phasial changes occurring in the ordinary age-hardening alloys where a small amount of a second phase is precipitated. The palladium-content alloys containing less than 25 atomic per cent palladium, which were aged at low temperatures, circa 300° C. for 15 min., contain the face-centered tetragonal phase plus the face-centered cubic phase, while those aged at higher temperatures—in the neighborhood of 450° C.—contain a body-centered tetragonal phase in addition to the two phases previously noted. The 25 atomic per cent palladium alloy, aged at 450° C. for 15 min., differs from those containing less palladium in that it contains the body-centered tetragonal phase and two face-

centered cubic phases. Upon further aging for 4 hr. at 400° C., one of the cubic phases changed to a face-centered tetragonal phase.

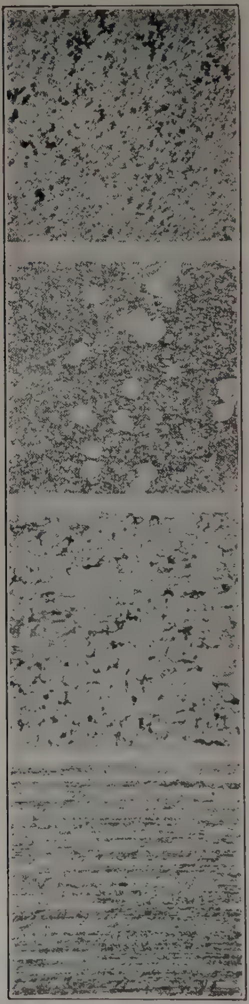

Fig. 1.—Microstructures of a 15 atomic per cent platinum alloy after quenching at 940°, 950°, 1175° and 1190° C. × 125.

The high-platinum-content alloys likewise contain a face-centered tetragonal phase and a face-centered cubic phase. The tetragonal phase is evidently derived from AuCu by the replacement of a portion of the gold by platinum, as was noted in connection with the chemical analysis of this phase.

8. The age-hardening of the alloy containing neither platinum nor palladium is due to the formation of a face-centered tetragonal phase. The alloys containing up to 25 atomic per cent palladium are hardened by the rather general transformation of the initially soft alpha solid solution into two new and probably rather distorted phases; namely, a face-centered tetragonal phase and a body-centered tetragonal phase. The latter may be regarded as a slightly distorted form of the normally body-centered cubic phase PdCu. The platinum-content alloys are hardened by the precipitation of a face-centered tetragonal phase. A detailed exposition of the complex processes involved in age-hardening has been given by Merica.[2]

Experimental Methods and Data

Alloys Studied.—Compositions of the alloys studied are indicated in Table 1, the samples being identical with those described in the previous paper. They were available in the form of 0.040-in. wire.

Determination of the Liquidus.—Cooling curves were run on all of the alloys, using melts of 45 grams each. A Pt-PtRh thermocouple protected by a very thin-walled protection tube was used in all cases. The melting was done in a hydrogen atmosphere, and the usual inverse rate curves were plotted. This procedure was entirely satisfactory for the gold and palladium alloys, but was quite unsuitable for the alloys containing 10 or more atomic per cent of platinum, because the liquidus arrest was ill defined and practically absent in the alloys containing either 15 or 20 atomic per cent of platinum, although the arrest due to the peritectic reaction was very evident. Satisfactory results were obtained with the latter alloys by melting 1 to 2-gram samples in a small closed-end quartz tube in a hydrogen atmosphere. These melts were held at chosen temperatures for 10 min., and were then water-quenched. The resulting bead was ground, polished and etched. Examination at 250 dia. was sufficient to indicate whether the alloy was wholly or only partly molten at the time of quenching. Fig. 1 shows the appearance of alloys containing 15 atomic per cent of platinum quenched from temperatures slightly below the solidus, between the liquidus and solidus and above the liquidus. The alloy quenched from 1190° C. was entirely liquid at the time of quenching, while the one quenched at 1175° C. contained some unmelted solid. These large unmelted crystals are the platinum-rich phase, which is denser than the liquid, hence they tend to settle to the lower portion of the melt if held at temperatures within the semi-solid region. It is probable that this behavior is responsible for some of the difficulties grouped under the classification of "segregation," which producers of these

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[2] P. D. Merica: The Age-hardening of Metals. *Trans.* A.I.M.E. (1932) **99**, 13.

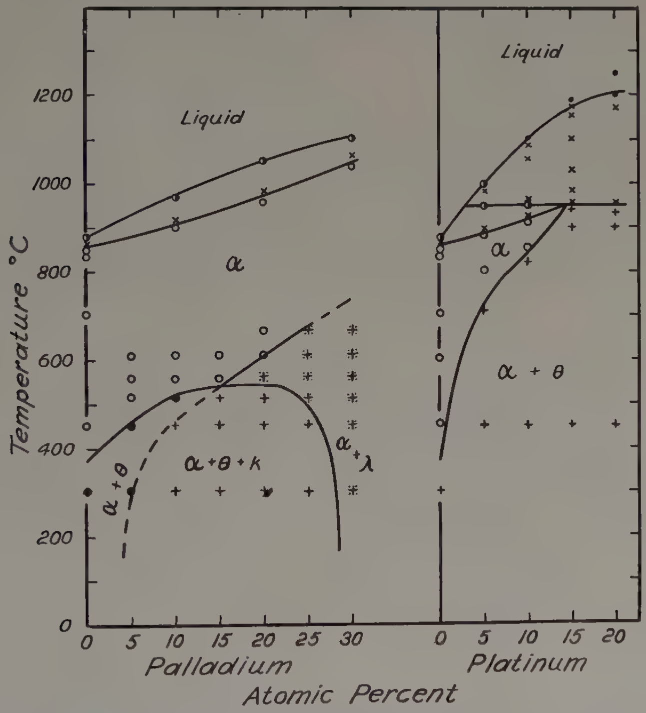


FIG. 2.—CONSTITUTIONAL DIAGRAMS OF THE PLATINUM AND PALLADIUM-CONTENT ALLOYS.

alloys have encountered and which appear to be due to attempts to cast such alloys below their real and hitherto unknown liquidus temperature, an error that might readily occur owing to the mobility of these alloys at temperatures appreciably below the true liquidus. The results of these experiments are indicated in Fig. 2.

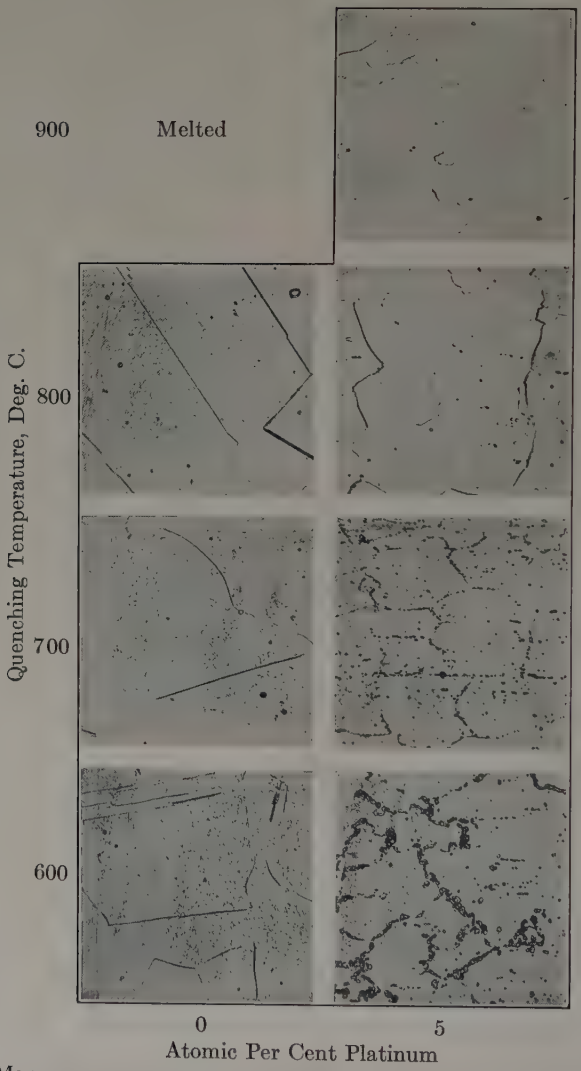


Fig. 3.—Microstructures of quenched platinum-content alloys. × 500.

Determination of the Solidus.—The solidus temperatures were obtained by quenching small samples at a suitable series of temperatures and subjecting them to metallographic examination at about 1000 dia. These results are embodied in Fig. 2. In spite of the fact that the rate of rise of the liquidus with the platinum metal content (on an atomic percentage basis) is almost three times as high for the platinum-content alloys as for the palladium-content alloys, the initial rate of rise of the solidus is almost the same for both. The increase in solidus temperature of the platinum-content alloys ceases at about 14 atomic per cent platinum, because of the occurrence of a peritectic reaction at 948° C. The solidus of the palladium-content alloys continues to rise throughout the range studied,

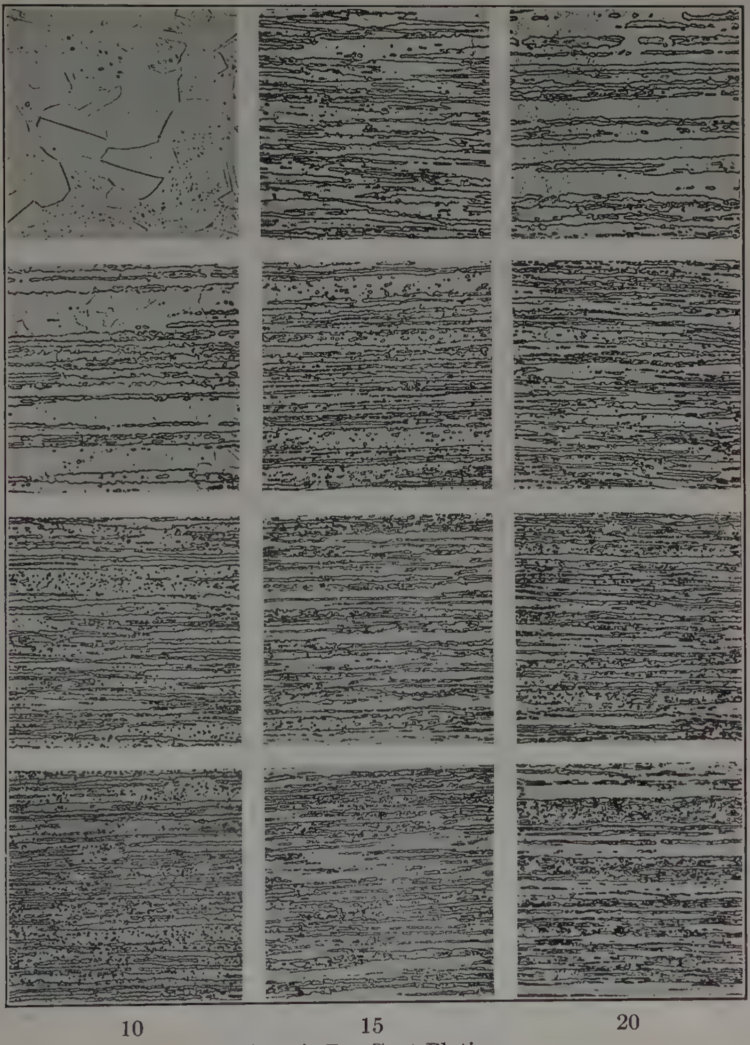


Fig. 3. *Continued*

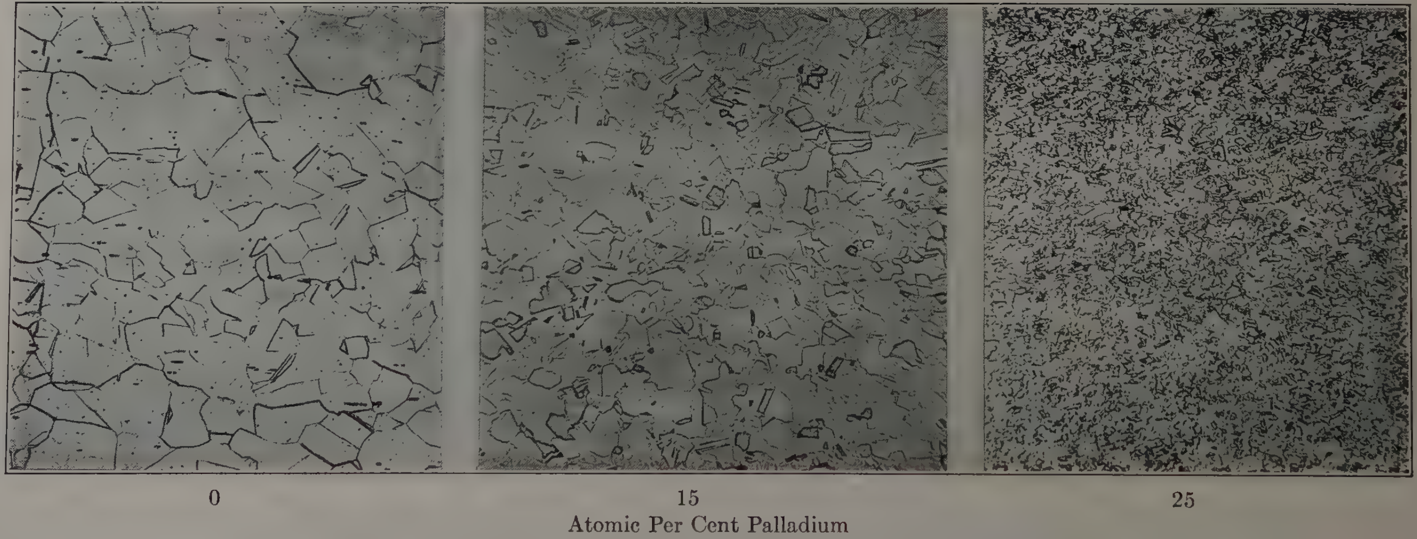


FIG. 4.—MICROSTRUCTURES OF PALLADIUM-CONTENT ALLOYS QUENCHED from 700° C. × 100.

and doubtless continues to the melting point of a 50 atomic per cent palladium alloy.

Microstructures of the Quenched Alloys.—Samples of the alloys of the platinum series 0.040 in. in diameter were annealed for 5 min. at temperatures ranging from 600° to 900° C., and were water-quenched. Owing to the extremely small grain size of the samples containing reasonable quantities of platinum, a magnification of 1000 was utilized in preparing the original photomicrographs shown in Fig. 3. The amount of excess phase, theta, increases with the platinum content and decreases with an increase in quenching temperature. The grain size, likewise, decreases markedly with an increase in platinum content. The presence of even traces of the excess platinum-rich phase, theta, seems to be extremely effective in restraining grain growth.

The influence of palladium upon the microstructure of the quenched alloys is shown in Fig. 4. These alloys, when quenched from 700° C., exhibit only a single phase up to 30 atomic per cent palladium, at least, and the grain size decreases with an increase in the palladium content, although this effect is less marked than in alloys containing platinum.

Effect of High Annealing Temperature Upon the Properties of the 5 Atomic Per Cent Platinum Alloy.—The tensile properties of the alloy containing 5 atomic per cent platinum as a function of quenching temperature are shown in Fig. 5. The microstructures of the quenched alloy correspond to those shown in Fig. 3. Little damage to properties results until the quenching temperature exceeds the solidus and some melting occurs; that is, until a quenching temperature of about 895° C. is approached.

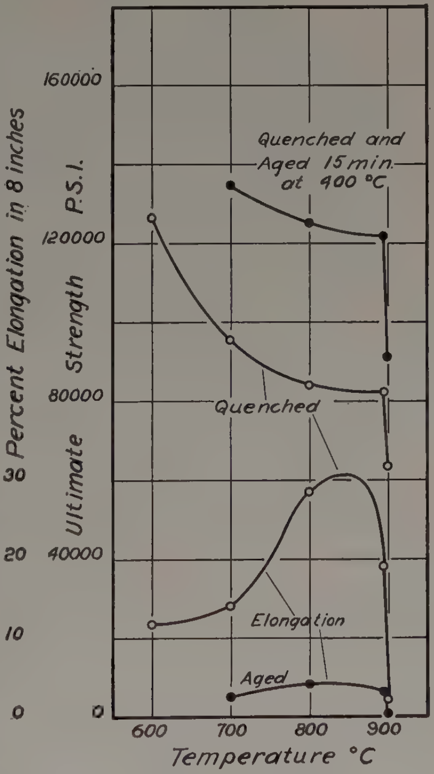


FIG. 5.—EFFECT OF QUENCHING TEMPERATURE ON THE PROPERTIES OF A QUENCHED, AND QUENCHED AND AGED, 5 ATOMIC PER CENT PLATINUM ALLOY.

Fig. 1 shows that in the 15 atomic per cent platinum alloy an exceedingly fine grain size is maintained up to the solidus temperature. This behavior is responsible for the maintenance of the high physical properties until a small amount of melting has occurred.

Excess Phase in the High-platinum-content Alloys.—As was noted above, the quenched high-platinum-content alloys usually exhibit a duplex structure, consisting of the ductile alpha phase and the platinum-content phase that we shall call theta. At a constant temperature, the amount of the theta phase increases with the platinum content. It was thought desirable to isolate and analyze this phase. A sample containing 15 atomic per cent platinum, which had been annealed at 700° C. for 5 min., was selected and was electrolyzed as anode in a 10 per cent KCN solution. By proceeding cautiously toward the end of the electrolysis and stopping the process while a small amount of unattacked core remained, it was found possible to isolate a gossamerlike "rope" in quantities sufficient for analysis. As in other residue methods, there is the possibility that some slight amount of attack upon the desired residual phase occurred during the process of separation and, in fact, it was found that if the electrolysis was continued after the core was wholly dissolved a brownish solution product resulted and the "rope" tended to disintegrate. The weights and analyses of the resulting products are given in Table 2. These results correspond closely to a phase, or compound, having the formula $AuPt_2Cu_3$. It appears that this phase is derived from the compound AuCu by the partial replacement of gold by platinum, but probably varies in composition with the temperature and composition of the alloy. This is compatible with the results of the X-ray studies discussed later in this communication.

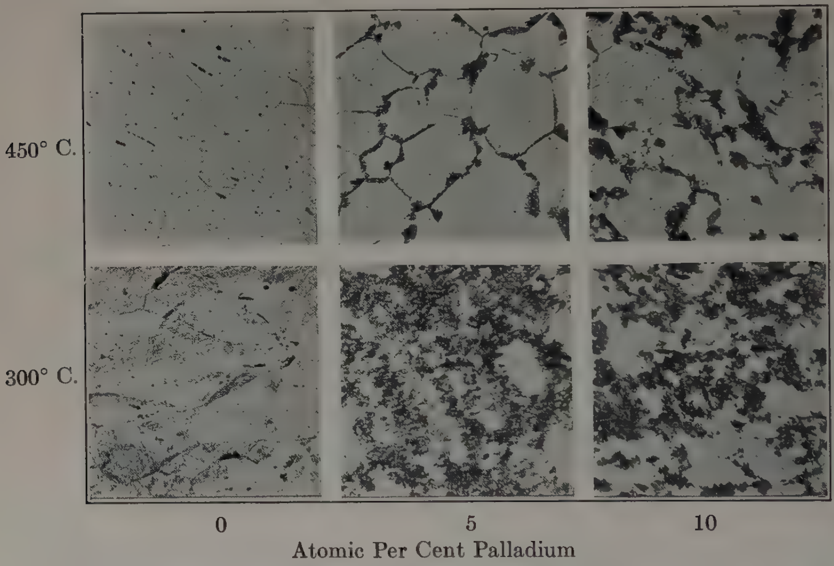


FIG. 6.—MICROSTRUCTURES OF PALLADIUM-CONTENT ALLOYS ANNEALED AT 300° AND 450° C. FOR 624 AND 100 HR., RESPECTIVELY, AND QUENCHED. × 125.

Variation in Solubility of High-platinum-content Phase, Theta, with Temperature.—In the alloys studied, the atomic percentage of gold and platinum was equal to 50 atomic per cent in all cases, and thus a determination of the thermal domain of homogeneous alloys as a function of the platinum content is fundamental to the design of alloys exhibiting the maximum efficiency in the utilization of platinum for producing the most effective combination of properties.

Samples were heated in vacuo at temperatures ranging from 600° to 850° C. for 6 hr., and were quenched and examined at 1000 dia. The

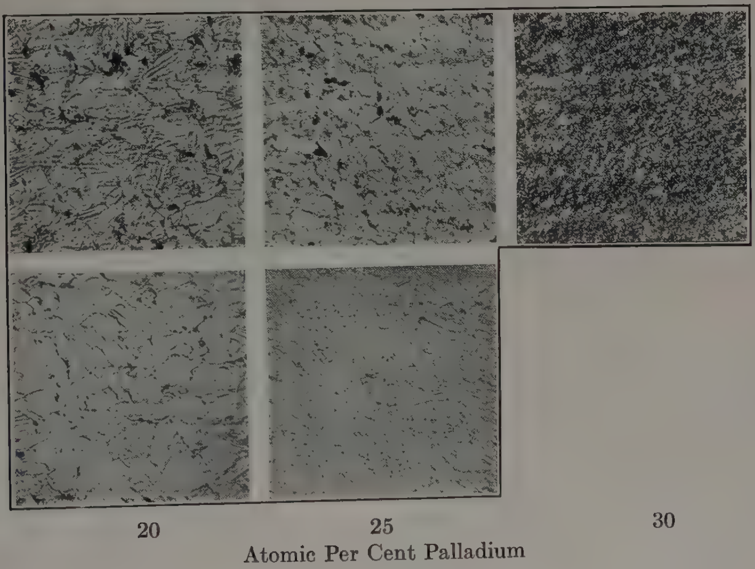


FIG. 6. *Continued*

TABLE 2.—*Weights and Analyses of Products of Electrolysis*

Sample anode in 10 per cent KCN solution: 15 atomic per cent Pt, annealed at 700° C. for 5 min. and quenched; total weight, 5.2495 grams

	Pt	Au	Ag	Cu
Weight per cent in residue	50.23	25.74	2.76	21.27
Atomic per cent in residue	34.43	17.45	3.42	44.70
Weight per cent in sample	21.1	49.6	15.5	13.3
Grams in sample	1.1176	2.607	0.813	0.698
Grams in residue	0.3256	0.167	0.018	0.138
Grams in alpha solid solution	0.7920	2.440	0.795	0.560
Weight per cent in alpha solid solution	17.26	53.18	17.34	12.22
Atomic per cent in alpha solid solution	12.43	37.90	22.62	27.05

samples heated at or below 450° C. were held from 100 to 624 hr. and then quenched. The solid solubility so determined is indicated in Fig. 2. The solubility of the platinum-content phase theta increases markedly with the temperature, and the alpha solid solution contains about 14 atomic per cent of platinum at the maximum solidus temperature (948° C.).

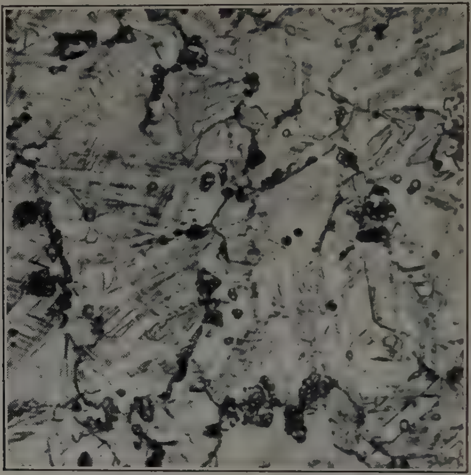


Fig. 7.—A 25 atomic per cent palladium alloy annealed 100 hr. at 450° C. and quenched. × 1000.

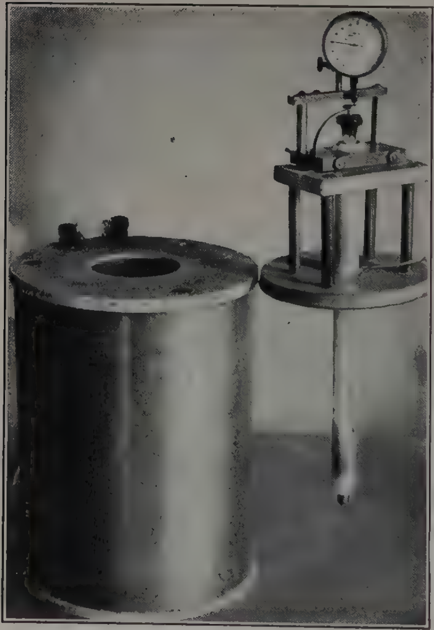


Fig. 8.—Dilatometer.

Determination of Domain of Palladium-containing Phases.—Samples of the palladium-content alloys were annealed at temperatures ranging from 300° to 665° C. Those at 300° and 450° C. were annealed 624 and 100 hr., respectively, while those at higher temperatures were annealed 25 hr. All were water-quenched. The samples employed had been previously annealed at either 600° or 700° C., and were subsequently strained to accelerate the attainment of equilibrium at the low temperatures. The microstructures of a few of these samples are shown in Fig. 6. At 300° C. the gold alloy contained alpha and a second phase, which has

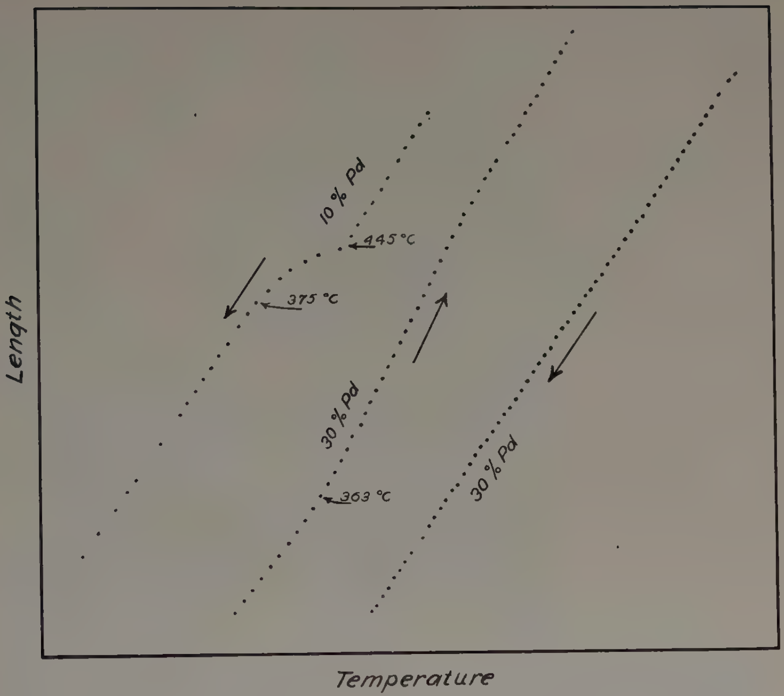


FIG. 9.—TYPICAL CURVES OBTAINED IN THE DILATOMETRIC ANALYSIS.

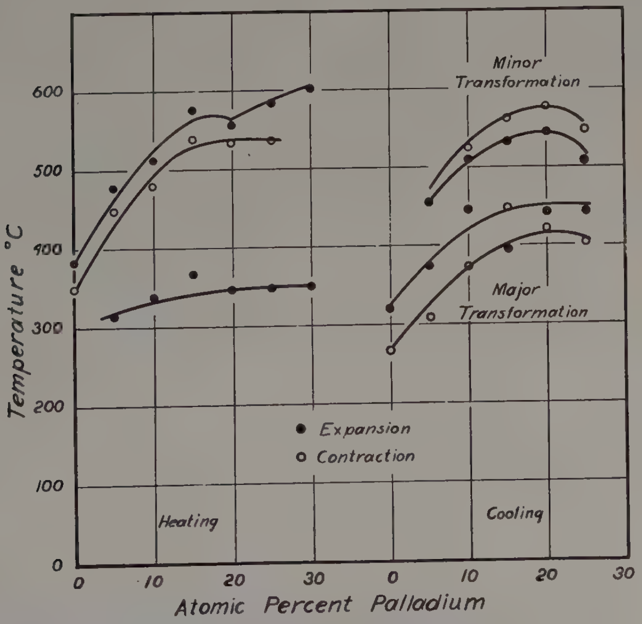


FIG. 10.—DIAGRAM OF THE DIMENSIONAL CHANGES OBSERVED BY DILATOMETRIC ANALYSIS.

been designated as theta. The latter had the same crystal form as the theta phase in the platinum-content alloys. The amount of theta decreased as the palladium increased from 5 to 25 atomic per cent. In spite of the fact that the microscope disclosed the presence of but two phases in the alloys containing from 10 to 20 atomic per cent palladium and only one phase in the 25 atomic per cent palladium alloy, X-ray analysis indicated that they contained alpha + theta + a second new phase, which

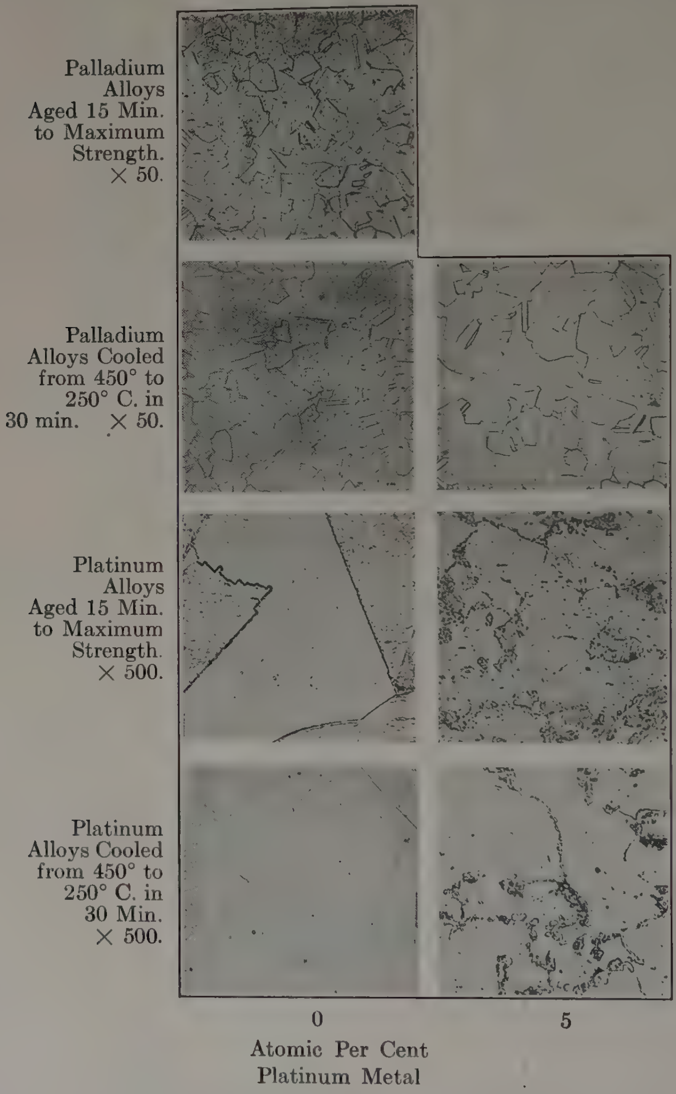
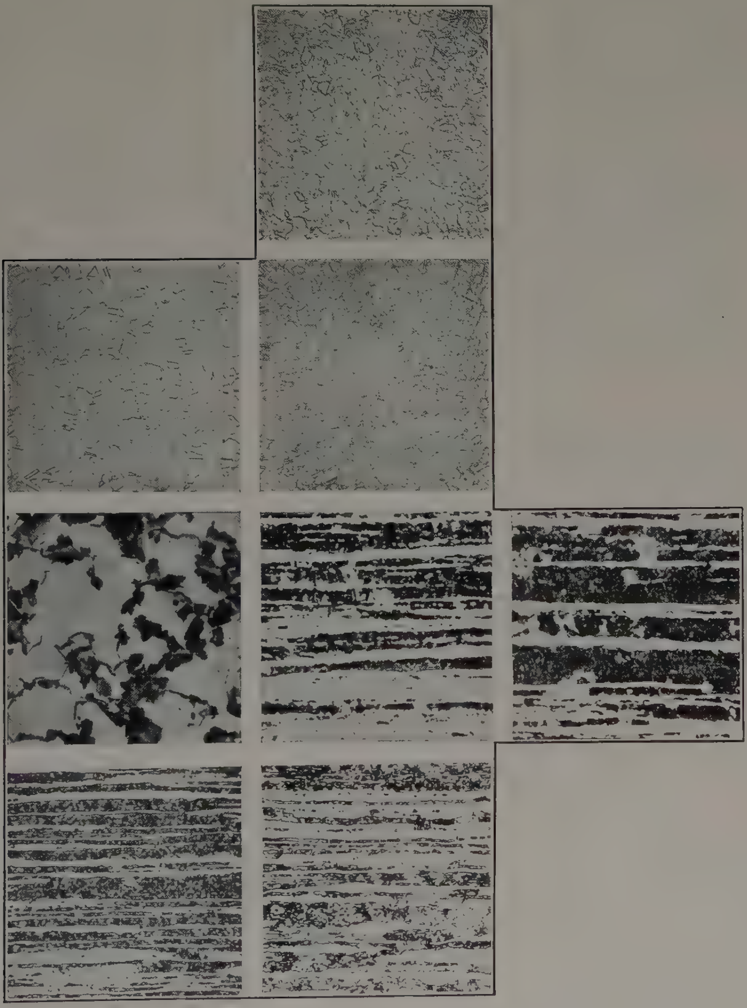

Palladium Alloys Aged 15 Min. to Maximum Strength. × 50.
Palladium Alloys Cooled from 450° to 250° C. in 30 min. × 50.
Platinum Alloys Aged 15 Min. to Maximum Strength. × 500.
Platinum Alloys Cooled from 450° to 250° C. in 30 Min. × 500.
0
5
Atomic Per Cent Platinum Metal

Fig. 11.—Microstructures of platinum and palladium-content alloys after their optimum aging treatment and the 450° to 250° C. slow cool treatment.

has been designated as kappa. The 30 atomic per cent alloy contained a finely divided mixture of alpha and a third new phase designated as lambda, the latter being identified by X-ray analysis.



Atomic Per Cent
Platinum Metal
FIG. 11. *Continued*

At 450° C. the 0 atomic per cent palladium-content alloy consisted entirely of alpha. With the addition of palladium up to 25 atomic per cent, microscopic and X-ray analyses showed the occurrence of the same phases as at 300° C.; namely, alpha + theta + kappa. The 30 atomic per cent palladium alloy contained alpha + lambda. Fig. 7 shows the appearance of the 25 atomic per cent palladium alloy quenched from 450° C. at a magnification of 1000 dia. The matrix of this alloy has a microstructure similar to a 50 atomic per cent gold gold-copper alloy studied by Haughton and Payne.[3] Their alloy was quenched at 400° C., *i. e.*, within the AuCu region.

At 515° C. the matrix of the alloys within the ternary field had a structure similar to the matrix of the alloy shown in Fig. 7. This must be alpha + theta. The kappa phase occurred as a clear globular constituent around the grains. The 30 atomic per cent palladium alloy contained alpha + globular lambda.

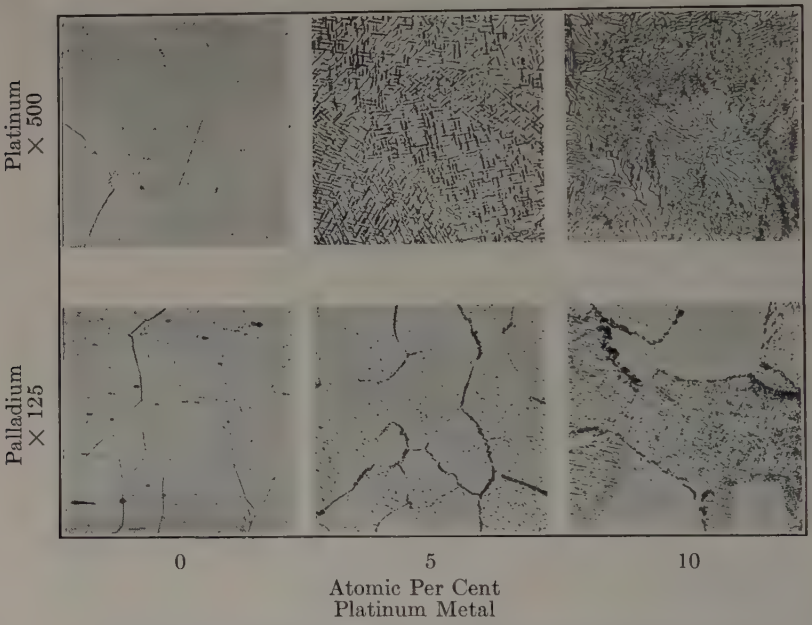


FIG. 12.—MICROSTRUCTURES OF PLATINUM AND PALLADIUM ALLOYS AFTER COOLING FROM 800° OR 900° C. TO ROOM TEMPERATURE IN 105 HOURS.

The alloys quenched at higher temperatures within the alpha + lambda field contained clear etching alpha (free from Widmanstätten markings) and globular lambda.

Dilatometric Studies on Palladium-content Alloys.—Owing to the shape of the solid-solid transformation, as inferred from the hardening results previously reported, and to the nature of the transformation, it was thought that these changes could best be followed by dilatometric methods. A suitable device (Fig. 8) was constructed to follow the length changes in small wire samples and was arranged so that the test wire was maintained under moderate tension during the thermal cycle.

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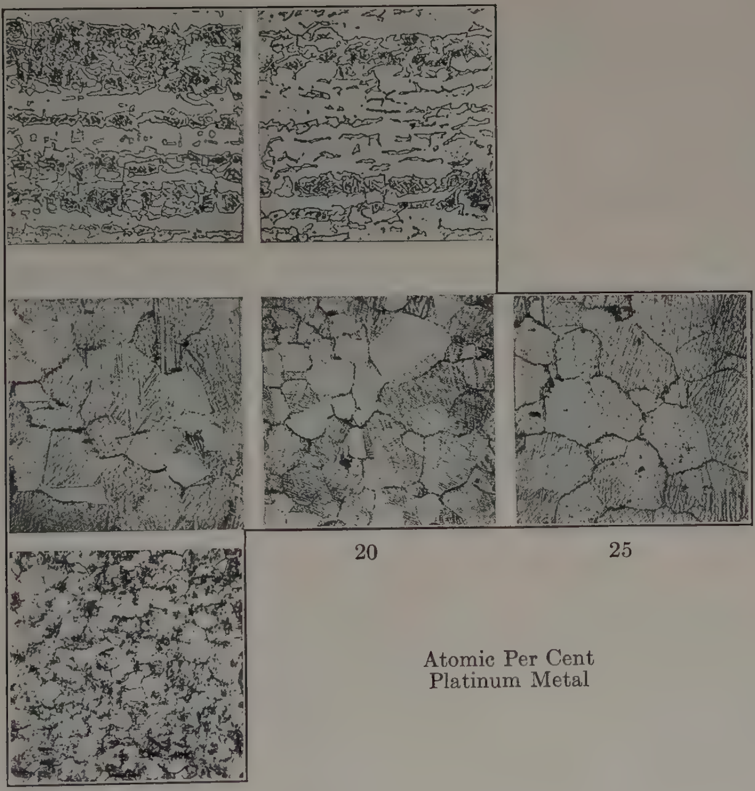
[3] J. L. Haughton and R. J. M. Payne: Transformations in Gold-Copper Alloys. *Jnl.* Inst. Metals (1931) **46**, 457.

Typical curves obtained with this apparatus are shown in Fig. 9. The heating rate employed was about 6° C. per minute, and the cooling rate 4° C. per minute. The samples employed were originally annealed for 4 hr. at either 800° or 900° C., depending upon the platinum-metal content, and were then slowly cooled to room temperature in 105 hours.



20

25

Atomic Per Cent
Platinum Metal

Two above 15
Lower one 30

FIG. 12. *Continued*

The results of these measurements are given in Fig. 10. It should be noted that the upper limits of the mixed fields are given for both heating and cooling. Owing to the marked hysteresis in the transformations, it seemed desirable to indicate them separately, so as to show the results that would be expected from various thermal cycles.

In order to determine which of the dimensional disturbances, observed on cooling, was associated with the hardening transformation, three sets of samples were annealed at 675° C. One set was quenched at 675° C., and the other two were cooled at the rate of 4° C. per minute, the same rate employed in the dilatometric work. A second set of alloys was quenched at 475° C., while the third was cooled to 330° C. and quenched. Hardness measurements were made on all of the samples, and it was found that while a very slight increase in hardness occurred on cooling from 675° to 475° C., the major increase in hardness was associated with the lower dimensional change.

The domains of the palladium-containing phases shown in Fig. 2 have been determined from the combined results of the microscopic, dilatometric and X-ray analyses. The ternary field alpha + theta + kappa is undoubtedly due to the overlapping of two basic transformations, one based upon AuCu and the other PdCu. The reasons for this interpretation are: (1) Only the alpha and theta phases, the latter being derived from the face-centered tetragonal phase AuCu, occurred in the alloy containing 0 atomic per cent palladium; (2) the lambda phase, which is based upon the body-centered cubic phase PdCu, and the alpha phase were present in the 30 atomic per cent palladium alloy; and (3) the alloys containing from 10 to 25 atomic per cent palladium contained the three phases, alpha + theta + kappa, which is body-centered tetragonal, or simply a body-centered cubic cell with one shortened side.

The lower limit of the alpha solid solution was determined by both dilatometric and microscopic analyses. The line at the left of the alpha + theta + kappa field was drawn to indicate the probable location of the boundary between the alpha + theta and alpha + theta + kappa fields, since no evidence of the presence of the kappa phase was observed in the X-ray diffraction patterns of the 0 and 5 atomic per cent palladium alloys. The boundary at the right of the alpha + theta + kappa field was determined by X-ray analysis.

Structures of the Age-hardened Alloys.—The microstructures of the alloys of the platinum series, after quenching from 900° C. (except for the alloys containing 0 and 5 atomic per cent platinum, which were quenched from 800° C.) and aging for 15 min. at a temperature producing the maximum strength in each alloy, and after annealing at 700° C. and applying the 450° to 250° slow cool treatment, are shown in Fig. 11. The presence of reasonable quantities of platinum causes the precipitate to assume a troostitic appearance, while the platinum-free alloy aged at the temperature producing the maximum strength (300° C. for 15 min. aging) shows little change in microstructure from that of the quenched sample. By increasing the aging temperature to 350° C. a rather faint Widmanstätten type of structure developed in this alloy. The palladium-content alloys exhibit the latter type of structure when aged at the temperature producing the maximum strength and after the 450° to 250° C. slow cool. Typical structures assumed by these alloys are shown in Fig. 11.

Samples of 0 and 5 atomic per cent platinum and 5 atomic per cent palladium were annealed for 4 hr. at 800° C., while the alloys containing larger amounts of platinum or palladium were annealed for 4 hr. at 900° C. All samples were cooled very slowly to room temperature, the cooling requiring about 105 hr. The structures resulting are shown in Fig. 12. It should be noted in consulting this plate that the initial magnification employed was 1000 dia. for the platinum alloys and 250 dia. for the palladium alloys.

X-Ray Studies Concerning the Constitution of the Alloys

Equilibrium Phases of the Palladium-content Alloys.—The diffraction spectra of the alloys containing up to 25 atomic per cent palladium, quenched from the alpha field—that is, from temperatures above 370° to 700° C., depending upon the palladium content—indicate that the alloys are wholly of the face-centered cubic type designated as alpha and characterized by a lattice constant ranging between 3.96 and 3.89Å. The lattice constant diminished with an increase in palladium content, as would be expected from the difference between the lattice constant of gold (4.07Å) and that of palladium (3.90Å).

The alloys containing between 10 and 25 atomic per cent of palladium annealed at 450° C. for 100 hr. were found to contain three phases; namely, a face-centered cubic (alpha), a face-centered tetragonal, designated as theta, with an axial ratio of 0.92, and a body-centered tetragonal, termed kappa, with an axial ratio of 0.96–0.98. After annealing at 300° C. for 624 hr. and quenching, the alloys containing 0 and 5 atomic per cent palladium contained only the face-centered cubic (alpha), and face-centered tetragonal (theta) phases. The diffraction patterns from the alloys containing from 10 to 25 atomic per cent of palladium, after heating at 300° C. for 624 hr. and quenching, were not well defined, but it appears that these three alloys contain the same phases as at 450° C.; namely, face-centered cubic (alpha), face-centered tetragonal (theta) and body-centered tetragonal (kappa). The alloy containing 30 atomic per cent palladium, after being heated at either 450° or 300° C., contained the face-centered cubic (alpha) and a new body-centered cubic phase (lambda).

The lattice dimension of the alpha phase present in the polyphase region is, in general, larger than that of the same phase in the region where alpha is the sole constituent due to the change in the composition of the residual alpha as the result of the formation of the new phases.

At 450° C. the a dimension of the face-centered tetragonal cell was about the same size as the parent alpha cell, except in the case of the 25 atomic per cent palladium alloy, which was much larger. The axial ratio of the body-centered tetragonal phase varied from 0.96 to 1.0 between 10 and 30 atomic per cent palladium. The *a* dimension decreased from 3.43 to 3.01Å, the latter being almost identical with that of PdCu, 2.99Å, determined by Johannson and Linde.[4] This presence of the body-centered tetragonal phase in the alloys containing 10 and 15 atomic per cent of palladium is inferred from the presence of faint lines in the diffraction patterns. The 25 and 30 atomic per cent palladium alloys gave patterns in which lines corresponding to the body-centered phases are quite strong. These relationships are shown in Fig. 13.

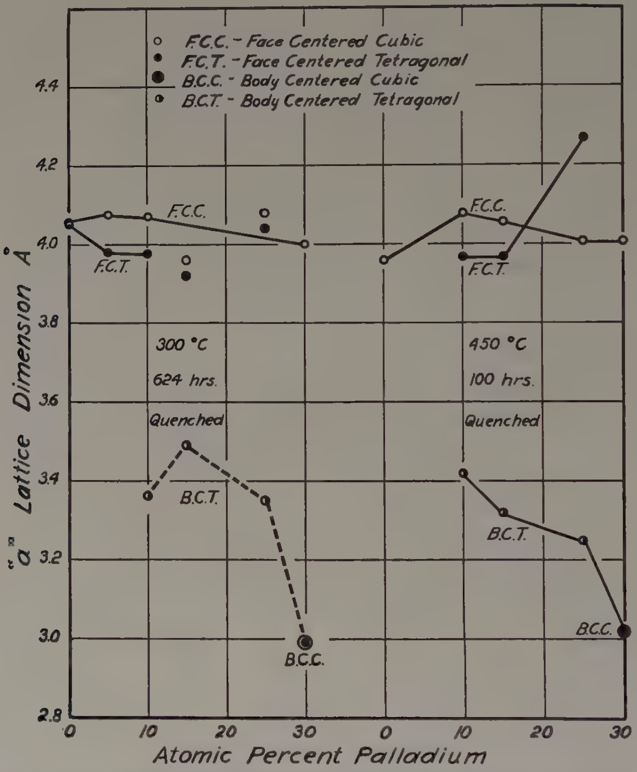


FIG. 13.—LATTICE DIMENSIONS OF THE HEAT-TREATED PALLADIUM-CONTENT ALLOYS.

Equilibrium Phases of the Platinum-content Alloys.—The 10 atomic per cent platinum alloy, quenched from 900° C., contained only a face-centered cubic alpha phase with a lattice parameter of 3.97Å. This constant computed from the theoretical density of the alloy was 3.98Å.

The 20 atomic per cent platinum alloy quenched from 900° C. was found to contain both the alpha face-centered cubic phase and a face-centered tetragonal phase, theta, with a c/a axial ratio of 0.98. It can be seen that this new phase is very close to being cubic. The presence of two phases in this alloy is entirely in accord with the results of the metallographic examination.

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[4] Johannson and Linde: Röntgenographic Determination of the Atomic Arrangement of AuCu and PdCu. *Ann d. Phys.* (1925) **78**, 439.

Upon cooling these alloys to room temperature, the tetragonal theta phase appeared in the 10 atomic per cent platinum alloy, and an increase in the amount of this phase was observed in the 20 atomic per cent platinum alloy. Associated with this change in the quantities of the phases present were changes in the cell dimensions. The face-centered cubic cell, alpha, increased in size in both alloys, and in the 20 atomic per cent platinum alloy the axial ratio c/a of the tetragonal phase theta decreased from 0.98 to 0.90 and the a dimension also decreased. These changes in the two phases are in accord with other observed facts, for as the solubility of the high platinum-content phase, theta, in the alpha decreased, the latter should become richer in gold and silver. (The analysis of the theta phase, given previously, showed it to contain very little silver.) This would cause an increase in the size of the cubic

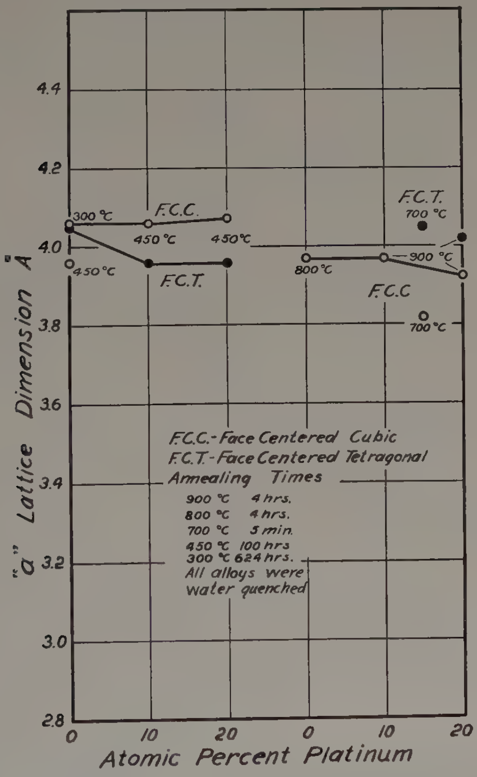


FIG. 14.—LATTICE DIMENSIONS OF THE HEAT-TREATED PLATINUM-CONTENT ALLOYS.

cell since gold, silver, and platinum have lattice parameters of 4.07, 4.08, and 3.93Å, respectively. By the same reasoning, the size of the platinum-content phase would be expected to decrease as the platinum content increased.

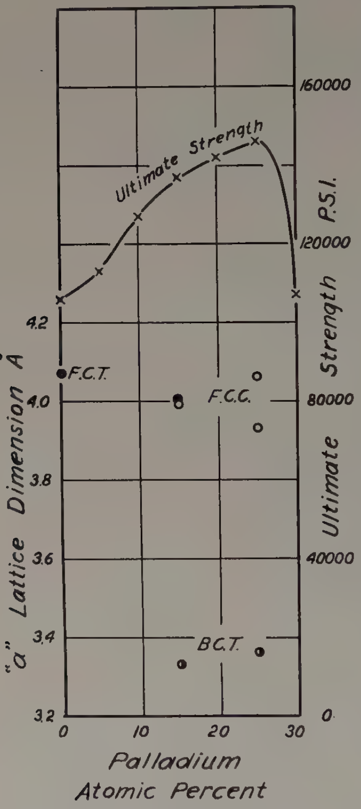


FIG. 15.—LATTICE DIMENSIONS AND ULTIMATE STRENGTH OF PALLADIUM ALLOYS AFTER BEING AGED AT THE TEMPERATURE PRODUCING MAXIMUM STRENGTH.

After annealing the 10 and 20 atomic per cent platinum alloys for 100 hr. at 450° C., an alpha phase with a lattice parameter of 4.06Å and a face-centered tetragonal phase with a lattice parameter of 3.96Å were present. This would indicate a high gold or silver content in the alpha phase resulting from the withdrawal of the copper.

The results on the platinum alloys are given in Fig. 14.

Phases Present in the Aged Palladium-content Alloys.—The structures of the phases present in the gold and palladium-content alloys, after being annealed at 700° C. for 5 min., quenched and aged 15 min. at their optimum aging temperatures (*i.e.*, the temperature producing the maximum strength) are given in Fig. 15. The ultimate strengths resulting from the same treatment are also given. It should be noted that the sample containing neither platinum nor palladium is the only alloy studied that changed completely from a cubic structure to a tetragonal structure upon aging. The 15 atomic per cent palladium alloy aged at 300° C., the lowest temperature at which an appreciable increase in strength occurred, contained a face-centered cubic and a face-centered tetragonal phase. No change from the as-quenched structure was observed in the 25 atomic per cent palladium alloy aged at 300° C. Upon aging at the optimum temperature, 450° C., the alloys containing 15 and 25 atomic per cent palladium were found to contain three phases: The first contained face-centered cubic + face-centered tetragonal + body-centered tetragonal phases, and the latter contained two face-centered cubic phases + a body-centered tetragonal phase. This checks admirably the deductions made in our previous study of the strength versus aging temperature in these alloys, which strongly suggested that two distinct phasial reactions were involved in the age-hardening transformations.

The changes in crystal structure and ultimate strength that occurred in a previously annealed 25 atomic per cent palladium alloy as the result of aging for 15 min. at temperatures from 300° to 500° C., are shown in Fig. 16. No change from the quenched state occurred at 300° C. At aging temperatures of 400° C., and above, a body-centered tetragonal phase developed and a new face-centered cubic phase possessing cell dimension differing from that of the residual parent solid solution made its appearance. Upon aging this alloy for a longer period of time at 400° C., the lattice dimensions varied as indicated in Fig. 17. After aging for 1 hr. the lattice constants of all three phases decreased from the values existing after 15 min. aging. After aging for 4 hr. the cell dimensions of the parent solid solution and the body-centered tetragonal phases continued to decrease; however, the new face-centered cubic phase that was observed in the sample aged for 1 hr. had been converted to a face-centered tetragonal form. This demonstrates that the face-centered tetragonal phase that formed in the palladium-content alloys is the more

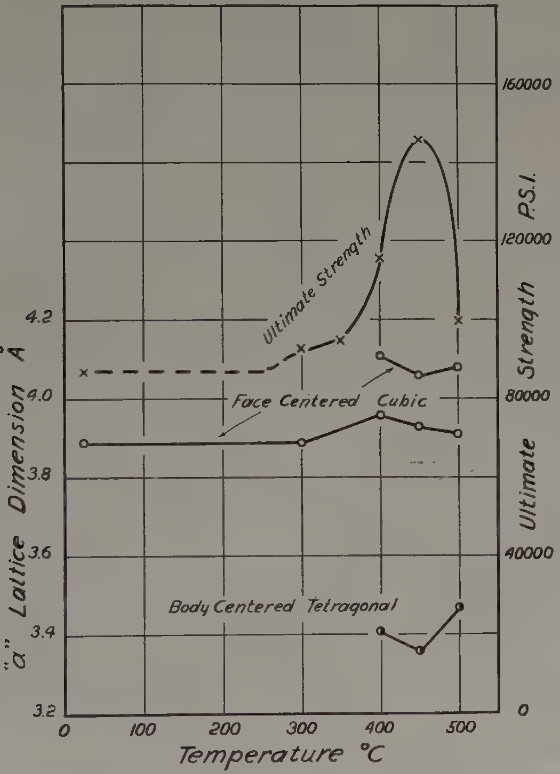


Fig. 16.—Changes in lattice dimensions and ultimate strength of a 25 atomic per cent palladium alloy after being quenched from 700° C. and aged at various temperatures for 15 minutes.

stable phase, and that the face-centered cubic phase was merely a transition phase.

Phases Present in the Aged Platinum-content Alloys.—The 10 atomic per cent platinum alloy annealed 5 min. at 700° C., quenched, and aged 15 min. at 500° C., contained the same phases as were present in a 10 atomic per cent platinum-content alloy that had been annealed at 450° C. for 100 hr. and then quenched; namely, a face-centered cubic phase and a face-centered tetragonal phase.

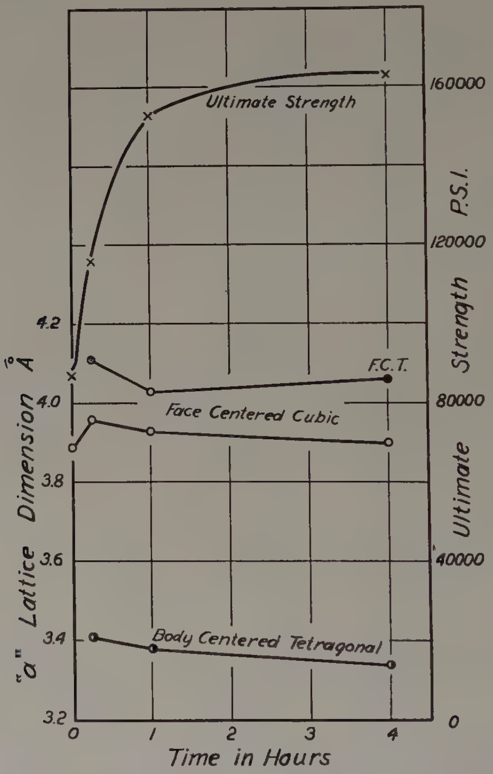
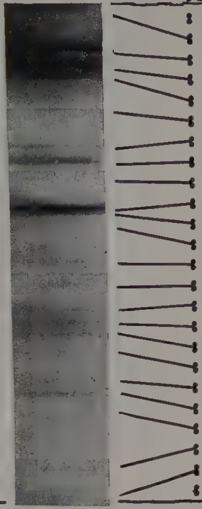


FIG. 17.—CHANGES IN LATTICE DIMENSIONS AND ULTIMATE STRENGTH OF A 25 ATOMIC PER CENT PALLADIUM ALLOY AFTER BEING QUENCHED FROM 700° C., AND AGED AT 400° C. FOR VARIOUS PERIODS OF TIME.

In the foregoing discussion of the aging of both the palladium and platinum alloys, very little has been said of the part played by silver. This metal is usually present in dental alloys in moderate amounts, and not only serves to reduce the cost of the alloy but also markedly improves the response to age-hardening. This is not only true for the alloys having an AuCu base but also those based upon PdCu. Due to the nearly equal lattice constants of Ag and Au, little information regarding the partition of silver between the various phases could be obtained from the X-ray

TABLE 3.—*X-ray Measurements on a 30 Atomic Per Cent Palladium Alloy Annealed 624 Hr. at 300° C. and Water-quenched*

Diffraction Pattern	Estimated Line Intensity	2θ	$\sin\theta$	$\sin^2\theta$	Face Centered Cubic		Body Centered Cubic			
					Plane	K	Plane	K	Superstructure	
									Plane	K
	1	13.55	0.118	0.0139					001	0.01390
	6	17.7	.154	.0237	111	0.00790				
	10	19.35	.168	.0282			110	0.01410		
	5	20.4	.177	.0314	200	.00785				
	1	23.59	.205	.0418					111	.01390
	5	27.49	.238	.0564			200	.01410		
	7	29.07	.251	.0629	220	.00786				
	1	30.75	.265	.0703					021	.01410
	10	33.75	.291	.0843			121	.01405		
	2	34.25	.294	.0867	113	.00788				
	1	35.8	.307	.0945	222	.00789				
	2	39.18	.336	.1124			220	.01405		
	1	41.5	.354	.1255	400	.00785				
	2	44.05	.375	.1406			103	.01406		
	2	45.54	.387	.1498	331	.00789				
	2	46.69	.396	.1570	240	.00785				
	2	48.55	.411	.1690			222	.01410		
	1	51.55	.435	.1891	242	.00788				
	4	52.75	.445	.1974			231	.01410		
	1	54.9	.461	.2125	151	.00787				
	1	60.26	.502	.2520	440	.00787				
	1	63.15	.524	.2742	351	.00785				

Face-centered cubic a = 4.00Å. Body-centered cubic a = 2.99Å.

data, except possibly in the case of the alpha phase of the low-temperature annealed platinum-content alloys.

OUTLINE OF METHOD EMPLOYED IN DETERMINING CRYSTALLOGRAPHIC DATA FROM X-RAY DIFFRACTION DATA

The method employed in determining the crystallographic habit of the phases from their diffraction patterns was identical with that described by Hull and Davey[5] and need not be discussed in detail at this time. It was thought, however, that a brief discussion of the "superstructure" or "uberstructure" lines and the presentation of typical calculations from two diffraction patterns would be of interest.

"Superstructure" lines are due to the periodic arrangements of like atoms, and are observed in phases existing in the "ordered" state. In the alloys studied these phases were the face-centered tetragonal and body-centered cubic. In the face-centered tetragonal phase, "superstructure" lines were observed for the 110, 201, 112, 221, 310, 203, 312, and 401 planes. The body-centered cubic phase "superstructure" lines were observed for the 001, 111, and 021 planes. These "superstructure" lines resulted from the same planes observed by Johannson and Linde[6] in their work on AuCu and PdCu, respectively.

Typical calculations based on X-ray diffraction data are given in Tables 3 and 4. Table 2 shows the calculations relating to a 30 atomic per cent palladium alloy annealed 624 hr. at 300° C. and quenched, while Table 3 shows the calculations for a 10 atomic per cent platinum alloy annealed 100 hr. at 450° C. and quenched.

A complete outline of the X-ray results obtained from all of the alloys studied is given in Table 4.

ACKNOWLEDGMENTS

The authors wish to express their thanks to Mr. A. J. Wadhams, Manager of the Development and Research Department, and to Dr. Paul D. Merica, Assistant to the President, of The International Nickel Co., Inc., for permission to publish the foregoing results; also to Dr. E. C. Bain and Dr. R. H. Aborn, of the Research Laboratories of the U. S. Steel Corporation, for their most effective assistance in connection with particular phases of the investigation.

APPENDIX.—METHOD UTILIZED IN PREPARATION OF SAMPLES FOR METALLOGRAPHIC EXAMINATION

The following method was employed in the preparation of the samples used for the preceding photomicrographs and is presented in the hope that

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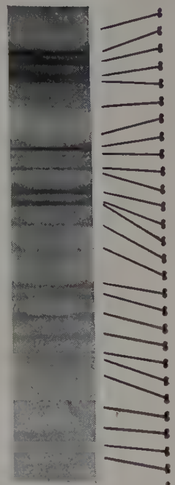
[5] Hull and Davey: Graphical Determination of Hexagonal and Tetragonal Crystal Structures from X-ray Data. *Phys. Rev.* (1921) **17**, 549–570.

[6] Reference of footnote 4.

TABLE 4.—*X-ray Measurements on a 10 Atomic Per Cent Platinum Alloy Annealed 100 Hr. at 450° C. and Water-quenched*

Diffraction Pattern	Estimated Line Intensity	2θ	$\sin\theta$	$\sin^2\theta$	Face Centered Cubic		Face Centered Tetragonal (c/a = 0.90)			
					Plane	K	Plane	K	Superstructure Plane	Superstructure K
	2	14.55	0.127	0.0161					110	0.00805
	10	17.40	.151	.0228	111	0.00760				
	10	18.55	.162	.0262			111	0.00809		
	5	20.15	.174	.0306	200	0.00765				
	4	20.65	.179	.0321			200	.00803		
	2	23.59	.205	.0418					201	0.00800
	2	27.14	.234	.0551					112	.00796
	9	28.69	.248	.0614	220	.00767				
	3	29.39	.253	.0643			220	.00804		
	6	30.90	.267	.0710			202	.00795		
	1	31.57	.272	.0740					221	.00801
	8	33.72	.290	.0841	131	.00765				
	5	34.92	.301	.0900			131	.00800		
	4	35.17	.303	.0914	222	.00762				
	5	37.43	.320	.1029			222	.00795		
	2	40.43	.345	.1194					312	.00800
	3	44.73	.380	.1448	133	.00761				
	3	46.28	.393	.1544			331	.00803		
	2	48.53	.411	.1689			402	.00806		
	2	50.67	.428	.1831	242	.00763				
	1	53.13	0.448	0.2000			242	0.00801		
	1	54.13	.454	.2070	151	0.00766				
	1	55.88	.469	.2197			151	.00805		
	1/2	59.40	.495	.2455	440	.00766				
	1	62.27	.517	.2674	351	.00764				
	1/2	64.42	.532	.2841			351	.00805		
	1/2	66.02	.545	.2966			442	.00804		

Face-centered cubic $a = 4.06$Å. Face-centered tetragonal $c/a = 0.90$; $a = 3.96$Å; $c = 3.56$Å.

TABLE 5.—*X-ray Diffraction Measurements*

Alloy		Treatment	Face-centered Cubic		Face-centered Tetragonal		Body-centered Tetragonal		Body-centered Cubic
Pd, Per Cent	Pt, Per Cent			a Ångstroms	c/a	a Ångstroms	c/a	a Ångstroms	a Ångstroms
0	0	100 hr. at 450° C. Quenched		3.96					
10		100 hr. at 450° C. Quenched		4.08	0.92	3.97	0.96	3.42	
15		100 hr. at 450° C. Quenched		4.06	0.92	3.97	0.98	3.32	
25		100 hr. at 450° C. Quenched		4.01	0.92	4.27	0.98	3.25	
30		100 hr. at 450° C. Quenched		4.01					3.01
0	0	624 hr. at 300° C. Quenched		4.06	0.89	4.05			
5		624 hr. at 300° C. Quenched		4.08	0.92	3.98			
10		624 hr. at 300° C. Quenched		4.07	0.92	3.98	0.97	3.36	
15		624 hr. at 300° C. Quenched		3.96	0.90	3.92	0.97	3.49	
25		624 hr. at 300° C. Quenched		4.08	0.90	4.04	0.97	3.35	
30		624 hr. at 300° C. Quenched		4.00					2.99
0	0	4 hr. at 800° C. Quenched		3.97					
0	0	4 hr. at 800° C. Slowly cooled to room temp.		4.04	0.89	4.04			
	10	100 hr. at 450° C. Quenched		4.06	0.90	3.96			
	20	100 hr. at 450° C. Quenched		4.07	0.90	3.96			
	10	4 hr. at 900° C. Quenched		3.97					
	10	4 hr. at 900° C. Slowly cooled to room temp.		4.06	0.90	3.98			
	10	5 min. at 900° C. Quenched. Aged 15 min. at 500° C.		4.065	0.91	3.965			
	15	5 min. at 700° C. Quenched		3.82	0.97	4.05			
	20	4 hr. at 900° C. Quenched		3.93	0.98	4.02			
	20	4 hr. at 900° C. Slowly cooled		4.11	0.90	4.01			
0	0	5 min. at 700° C. Quenched. Aged 15 min. at 300° C.			0.94	4.07			
15		5 min. at 700° C. Quenched. Aged 15 min. at 300° C.		3.94	0.98	4.09			
15		5 min. at 700° C. Quenched. Aged 15 min. at 450° C.		3.99	0.90	4.00	0.97	3.33	
25		5 min. at 700° C. Quenched		3.89					
25		5 min. at 700° C. Quenched. Aged 15 min. at 300° C.		3.89					
25		5 min. at 700° C. Quenched. Aged 15 min. at 400° C.	New 4.11	3.96			0.96	3.41	
25		5 min. at 700° C. Quenched. Aged 1 hr. at 400° C.	4.03	3.93			0.95	3.38	
25		5 min. at 700° C. Quenched. Aged 4 hr. at 400° C.		3.90	0.98	4.06	0.95	3.34	
25		5 min. at 700° C. Quenched. Aged 15 min. at 450° C.	4.06	3.93			0.95	3.36	
25		5 min. at 700° C. Quenched. Aged 15 min. at 500° C.	4.08	3.91			0.93	3.47	

it may prove of value to others engaged in the study of precious-metal alloys, in view of the fact that it is both rapid and effective.

The specimens were mounted in "hard" DeKhotinsky cement by carefully heating the cement with a hot iron, being careful not to heat it excessively, and allowing the molten cement to drip around the sample, which is surrounded by a split ring that is removed prior to grinding and polishing.

The mounted specimen was ground flat upon a series of rotating disks covered with carborundum papers graded as follows: 180–240–320–400. Finishing on a slightly finer paper might be better, but finer and otherwise suitable papers were not available.

The ground sample was then rough polished on a wet wheel covered with a sturdy broadcloth, charged with the American Optical Company's M-303 abrasive. This is a sharply graded material, which has been found to fit in nicely with the rest of the cycle. Final polishing was done on a wet broadcloth wheel charged with alumina levigated by Rodda's[7] method, utilizing material that settles not faster than ¼ in. per hour.

Etching was done by brushing with a mixture of equal parts of a 10 per cent solution of potassium cyanide and a 10 per cent solution of ammonium persulfate. The two solutions keep reasonably well, but the mixture spoils very rapidly. The etching time required varies with the alloy and the heat treatment, but is usually in the neighborhood of 10 seconds.

This reagent was developed for another purpose about 10 years ago by M. C. Jewett, a former associate of one of the authors. This reagent has proved to be generally useful as a metallographic etchant for precious-metal alloys, except for the extremely resistant platinum and palladium alloys which normally require a more drastic reagent.

About 10 min. is required to mount, grind, and polish a specimen by this procedure.

DISCUSSION

(Frederic E. Carter presiding)

C. S. Sivil, Newark, N. J.—I congratulate the authors on their courage in investigating two five-component systems simultaneously. The phase relations in such systems are very complicated, and even one such alloy series is to the average metallographer as the spider was to Miss Muffet. Unfortunately, most dental alloys are such spiders, they start off as a disarmingly simple binary or ternary alloy, but before they reach the mouth most of the periodic table has been dragged into their net. This state of affairs is, to say the least, regrettable and it is my opinion that we should attempt to develop the desired properties in alloys that are somewhat simpler in constitution. The dentist now knows enough of the desired properties to be able to give a guiding specification to the metallurgist, and knowledge of alloy building and also age-hardening phenomena has increased to such a point that it should not be impossible to design moderately simple alloys.

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[7] J. L. Rodda: Preparation of Graded Abrasives for Metallographic Polishing. *Trans.* A. I. M. E. (1932) **99**, 149.

Figs. 2, 3 and 5 when considered together offer certain points of interest. In Fig. 2 the temperature of 900° is, for the 5 per cent Pt alloy, about 15° above the solidus. The photomicrograph of this alloy in Fig. 3 does not indicate that the alloy was in a partly molten condition, while Fig. 5 shows clearly that some such change has taken place. It is possible that the five-minute annealing time is not sufficiently long to insure attainment either of equilibrium or even of the temperature. It is also possible that owing to the method of placing the samples in the furnace they did not all attain the same temperature. This, for instance, might possibly occur if the samples were placed in the furnace in a tight bundle. The third explanation is that the tensile strength is a more sensitive method of determining the solidus than the examination of quenched samples by means of the microscope. The determination of the tensile strength is certainly much less arduous than the preparation and examination of a microsection.

There is one dental point that is well brought out by this paper. The residual material after the potassium cyanide electrolysis is the hardening constituent and apparently is more chemically resistant than the alloy. This is important in dental work. The use of a base metal to produce age-hardening, as, for instance, tin with gold-palladium alloys, results in an alloy that oxidizes readily after being age-hardened. The oxidation seems to be due to the presence of a tin-palladium compound. Before age-hardening the alloy is resistant to such action. So there appears to be a distinct advantage in the use of a noble-metal hardener.

The authors extended the use of the method of determination of the solidus to the determination of the liquidus most ingeniously. If the method is of reasonable accuracy it affords a simpler means for the determination of the phase diagrams of solders and such alloys with a large interval between the liquidus and solidus.

H. E. Stauss, Newark, N. J. (written discussion).—The authors have been devoting a great deal of time to placing dental alloys on a sound metallurgical basis. It is well known that dental alloys owe their peculiar complexity to two tendencies—one to produce a good alloy and one to produce a low-priced alloy. It is to be hoped that in the near future alloys can be made and tested without those who have poor teeth being the only testing equipment.

The X-ray data presented by the authors is rather complex, but again shows the value of X-ray analysis in metallurgy. Probably in connection with their discussion of superstructures they do not give sufficient credit to the copper in the alloys, even though they are primarily interested in the role of the platinum metals. From the superstructures of the palladium alloys they were able to establish the presence of two metallic compounds, gold-copper and palladium-copper, and their results indicate that in the case of the palladium alloys it is the palladium-copper that causes the great strength of the hardened alloy. There seems to be no reason to doubt that if the authors had studied the superstructure of the platinum alloys, they would have found that the hardening element was platinum-copper. Thus later work is now vindicating the old rule of thumb dental alloys; but what is more important, it also holds out hope that more correctly proportioned alloys may be developed in the future.

G. Masing, Berlin, Germany (written discussion).—As this paper deals with quaternary alloys, the exact discussion of the equilibrium diagrams and of the constitutional conditions of the age-hardening reaction is extremely difficult. It may be assumed that the constitutional diagrams Fig. 2 of the paper are only provisional and that some complications may exist. Nevertheless the experiments of the authors offer a number of conclusions that are of general interest from the point of the theory of age-hardening.

The alloys containing palladium are very interesting because they contain a compound analogous to the copper-gold compound. I believe it is still an open question whether the age-hardening of these alloys is due to the precipitation in the ordinary sense of the word or to *transformations* leading to the formation of regular atomic arrangements. The mechanism of the latter as connected with hardening has not yet been fully investigated and it will be worth while to pursue it still more in detail, perhaps with the alloys investigated by the authors, as one may expect it to lead to results interesting both from the theoretical and the practical point of view.

The alloys containing platinum, while conforming in behavior to the general rules of age-hardening, are interesting in connection with the phase to which the authors ascribe the formula $AuPt_2Cu_3$. It is striking that the copper content of this phase is 50 atomic per cent as in the compound CuAu, and the authors suggest indeed that it is derived from the latter by partial replacement of gold by platinum. If that be true, one must assume that the distribution of the gold and platinum atoms is a random one, because otherwise it would be scarcely possible to work out a distribution in accordance with the symmetry of the space lattice. It is to be expected, therefore, that the ratio of gold to platinum may change by forming solid solutions.

It is very interesting to note that, while the gold atoms can be replaced by others, the copper atoms seem to be fixed in their positions. Perhaps this may be related with the fact that there exists in the binary alloys of copper with gold a second compound Cu_3Au, in which a part of the gold atoms may be considered to be replaced by copper, while a similar compound Au_3Cu is unknown.

Further investigation of problems concerning these compounds must lead to interesting results. An exact determination of the copper content of the excess phase is desirable to confirm definitely the view of the authors, as we know that generally the residual analysis alone is far from giving reliable results.

E. M. Wise and J. T. Eash (written discussion).—The remarks of Mr. Sivil are appreciated and his desire for the simplification of dental alloys is reasonable. However, a rather careful study of the simpler systems has indicated that the reliable attainment of high properties generally necessitates recourse to alloys at least as complex as those studied by the authors and frequently requires the co-presence of both platinum and palladium. An exception to this is found in the palladium silver-copper alloys which, despite their simplicity, develop remarkably high strengths.

In connection with the study of the hardenable platinum metal content alloys, it must be recognized that the domain of the hardenable alloys is a function of the copper to silver ratio and of the precious-metal content. In the alloys studied—namely, those containing about 30 atomic per cent copper—the hardening region terminates where the precious-metal content becomes appreciably greater than 55 atomic per cent in alloys containing equiatomic percentages of palladium and gold.

Further complications arise in connection with alloys to be used for dental castings. The basic casting alloys are much the same as those used in wrought form except that the desired melting point is usually lower. They may also contain certain small additions to promote solidity, and traces of other metals of the platinum group such as rhodium and ruthenium may be added to refine the grain size of the casting.

With regard to the solidus of the 5 per cent platinum alloys, our observations indicate that it lies between 885° and 895° C. The photomicrograph in Fig. 3 was taken from a sample annealed close to 895° C. and shows no fusion. The methods of heating employed were indicated in part II of this research, and involved the heating of specimens in a special rack in juxtaposition with a thermocouple of approximately the same diameter as the specimen and possessing heating vs. time characteristic similar to the specimen. Tensile tests are valuable but consume large quantities of material and time, and if made on wires of 12-in. length require great care in the construction and operation of the furnace to secure the necessary accuracy in temperature throughout the gage length of the specimen. The metallographic specimens can be short and require only about 10 min. for mounting, polishing, etching, and hence the examination of quenched specimens is not unduly slow and the results are clear cut if a sufficiently high magnification is employed. The quenching method employed for determining the liquidus of the high-platinum alloys works well, and if a vertical section of the bead is examined no difficulty arises in connection with the accurate determination of the liquidus. The results of this method and of the orthodox thermal method were checked against each other with satisfactory results in a low-platinum alloy where the thermal method was usable.

The advantages of the noble-metal hardeners in maintaining a high level of corrosion resistance, regardless of the heat treatment, is important and should be given thoughtful consideration. A most striking example of loss in nobility resulting from base-metal hardeners occurs in the gold-nickel alloys, for it has been found that an 18-kt. gold-nickel alloy will lose its nobility almost completely after being heated for some time at an intermediate temperature. This loss in nobility is due to the rejection of a reactive phase.

The remarks of Dr. Stauss on the testing of dental alloys and of the importance of keeping the cost low are pertinent. The favorable influence of the platinum metals upon the cost of dental alloys per unit of strength received attention in a previous communication.[8]

With regard to the phases present in the alloys after heat treatment, it must be recognized that the phases existing after short-time heat treatment differ in lattice parameter from the equilibrium phases and that in the case of the 25 atomic per cent palladium alloy, the aged material contains a phase not found under equilibrium conditions. Reference to the text and the diagrams will make these matters evident.

In the previous communication,[9] the fact that PdAgCu alloys of appropriate composition could be effectively age-hardened was disclosed. From this work it is evident that the presence of AuCu is by no means essential to the age-hardening process.

With regard to the hardening of the platinum-content alloys, it is evident that several changes occur simultaneously. As the temperature is lowered, the solubility of the theta phase in the alpha decreases, the lattice parameter of the alpha increases, the c/a ratio of the theta lattice decreases and the a dimension of theta decreases.

The discusser has apparently overlooked the fact that the superstructure lines of the platinum content alloys were actually determined and were found to differ from those which have been reported for platinum-copper. It must further be emphasized that the presence or the nature of the superstructure lines was not the sole basis for identifying the several phases present.

The remarks of Dr. Masing are worthy of thoughtful consideration. It is evident that the graphic presentation of the results of the study of a quaternary, or if zinc be considered, a quinary system, is not easy, and is only possible when the number of variables has been reduced. Furthermore, it is evident that the traces of the phase boundaries shown in our equilibrium diagrams represent the intersection of a plane with a surface which is by no means normal to the plane. As a result, the change in the amounts of the phases present resulting from a small change in either temperature or the gold to platinum metal ratio may be fairly small. Furthermore, the rate of formation and coalescence of certain of the phases is low. These factors, coupled with the necessity of relying largely upon X-ray diffraction patterns for the identification of the phases, renders the determination of the phasial domains a matter of considerable difficulty. It is hoped that better means for identifying these phases may be evolved by those concerned with precious-metal alloys. It would not be surprising if further complications were found in the platinum-content alloys, but the results we have presented are in conformity with all the data we have obtained, and certainly cover the essential features of alloys of practicable composition.

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[8] The Role of the Platinum Metals in Dental Alloys. *Trans.* A. I. M. E. (1932) **99**, 383, sec. II.

[9] Reference of footnote 8, sec. I.

With regard to the nature of the hardening reaction, it does appear that in the case of the palladium-content alloys at least the reaction is more nearly akin to the martensitic transformation than to the duralumin reaction.

Too much weight should not be attached to the particular ratios of gold, platinum and copper found in the phase isolated by anodic solution, for, as stated by the authors, it is believed that this phase is the result of the partial replacement of gold in AuCu by platinum, and its composition may change to some extent with the temperature and with the composition of the matrix. It has been found that an alloy of the composition $AuPt_2Cu_3$ is actually a homogeneous solid solution with a face-centered tetragonal structure having a c/a ratio of 0.98. The sample and the heat treatment employed in the preparation of the specimen employed as anode were selected primarily to indicate the composition of the excess phase frequently present in commercial dental alloys after the usual annealing treatments. As far as the residue method itself is concerned, due care must be exercised in conducting the anodic solution to avoid grossly erroneous results.

Thermal Expansivity of Aluminum Alloys

By L. W. Kempf,* Cleveland, Ohio

(New York Meeting, February, 1933)

The thermal expansion characteristics of aluminum alloys have been examined by several investigators, among whom may be mentioned Shakespear,[1] Schulz,[2] Hidnert,[3] Hidnert and Sweeney[4] and McCullough.[5] Shakespear compared the expansion of a series of aluminum alloys containing 14 per cent copper, with separate additions of about 1 per cent each of manganese, tin and zinc with that of pure copper. Schulz examined the expansion of aluminum and zinc and some aluminum-zinc alloys. Hidnert determined with a high degree of precision the expansion characteristics of pure aluminum, some aluminum-copper, aluminum-zinc, aluminum-silicon and some commercial alloys. Hidnert and Sweeney examined the expansion characteristics of aluminum-beryllium alloys. McCullough, by an interferometer method, determined the expansivity of some aluminum-copper, aluminum-magnesium, aluminum-iron, aluminum-nickel, aluminum-silicon and aluminum-manganese alloys.

Incidental to an investigation carried out during the past six years and leading to the development and exploitation of an aluminum piston alloy of relatively low thermal expansivity, the expansion characteristics of a wide variety of alloys were examined. Some of the data which might be of general interest are gathered in this paper.

Experimental Procedure

The apparatus used was essentially similar to those developed by the Bureau of Standards[6] and Howard Scott,[7] with a few minor changes for expediency. The specimen was approximately 4 in. long and the differential length changes between specimen and the quartz tube were determined by means of the same type of indicator used by Scott. Length changes can be read directly to 0.0001 in. and can be estimated to 0.00005 in. The apparatus was so disposed as to occupy the central portion of a vertical closed end electric furnace about 14 in. long. The temperature of the specimen was determined by means of a 22-gage calibrated copper-constantan thermocouple wedged into a drilled hole midway between the ends of the specimen. The voltage set up by the thermocouple was measured with a Leeds & Northrup type K potentiometer. Measurements were made at intervals between room temperature and about 300° C. Heating was carried out at a rate of about 1° C. per minute. The original length of the specimens was measured to 0.0001 in. by means of micrometer calipers.

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* Aluminum Research Laboratories, Aluminum Co. of America.

[1] Reports of the Light Alloys Committee, 48. National Advisory Committee for Aeronautics, June, 1931.

[2] *Phys. Ztsch.* (1921) **22,** 403.

[3] U. S. Bur. Stds. *Sci. Paper* 497 (1925).

[4] U. S. Bur. Stds. *Sci. Paper* 565 (1927).

[5] *Physics* (Sept. 8, 1931) **1,** 334.

[6] U. S. Bur. Stds. *Tech. News Bull.* 123 (1927) 2.

[7] *Trans.* Amer. Soc. Steel Treat. (1928) **13,** 829.

Scott completely discussed the errors incidental to this method of determination. As he indicates, one of the largest variable errors lies in the angle between the indicator arm and the normal to the direction of the expansion being measured. The indicator was brazed to a bracket and clamp which was used to secure it to the quartz tube. The bottom of the bracket assembly was ground to a plane surface normal to the direction of linear expansion. It therefore became possible to calibrate the indicator by removing the entire clamp assembly, placing it on a plane surface and reading from the dial the displacement of the indicator level by various combinations of Johannson gage blocks.

The apparent expansion of specimens observed in this type of apparatus is of course lower than the true by the expansion of the same length of silica. The tabulated data of the expansion curves give differential expansion but all coefficients of expansion have been corrected for the expansion of silica as determined by Souder and Hidnert.[8] The correction is applied by calculating an apparent coefficient of expansion from the observed data and adding to this the value for the coefficient of expansion of silica. The value for the coefficient of expansion of silica used in all corrections regardless of temperature range is 0.5×10^{-6}. The calculations of coefficients are based upon values for expansion interpolated at the temperatures concerned from smooth curves drawn through the plotted observed values.

The alloys investigated were cast in the form of cylinders about ⅜ in. in diameter in graphite molds. All specimens were annealed 20 hr. at 225° C. followed by air cooling to room temperature before the expansivity tests. Alloys were made from pure aluminum, cathode copper, electrolytic nickel, pure refined silicon, Armco iron, pure tungsten and molybdenum, and aluminum-chromium rich alloy.

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[8] U. S. Bur. Stds. *Sci. Paper* 524.

TABLE 1.—*Comparison of Determinations on Similar Materials Made by the Bureau of Standards and the Aluminum Research Laboratories*[a]

Sample No.	Percentage Composition					Coefficients of Thermal Expansion (to be multiplied by 10^{-6})							
						20°–100° C.		20°–200° C.		20°–250° C.		20°–300° C.	
	Cu	Fe	Si	Mn	Ni	A.R.L.	B.S.	A.R.L.	B.S.	A.R.L.	B.S.	A.R.L.	B.S.
4209	0.15	0.76	13.08			19.6	19.7	20.3	20.1	20.6	20.6	21.4	21.3
4284	3.14	0.84	19.30	1.08	4.18	16.7	16.6	17.4	17.0	17.7	17.3	18.0	17.8
4284–2d run	3.14	0.84	19.30	1.08	4.18	16.7		17.1		17.6		18.0	
99.95 per cent Al						23.4	23.8	24.6	24.7	24.9	25.2	25.3	25.7

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[a] The Bureau of Standards and Aluminum Research Laboratories specimens of samples 4209 and 4284 were from the same melt. The specimens of 99.95 per cent aluminum were of different origins.

RESULTS OF EXPERIMENTS

Several typical expansion curves are shown in Fig. 1, with the corresponding data in Table 1. The curves from duplicate runs of sample 4284 are shown.

A number of samples were available, which were duplicates of specimens cast from the same melt, the coefficients of expansion of which had been determined in 1926 by Hidnert and Sweeney, of the Bureau of Standards, using precision methods. These samples were prepared in the Aluminum Research Laboratories and were annealed at 400° C. for 1 hr. followed by cooling slowly to room temperature. The data in Table 1 show that the coefficients of expansion of companion bars determined by the Aluminum Research Laboratories and the Bureau of Standards agree very closely. A specimen was also available, sample 5542, the expansivity of which had been determined at the Bureau of Standards. This

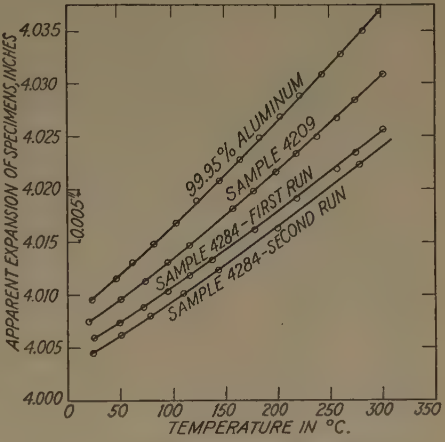

FIG. 1.—TYPICAL EXPANSION-TEMPERATURE CURVES.

Sample 4209, 13 per cent silicon; sample 4284, 3 per cent copper, 0.8 iron, 19 silicon, 1 manganese, 4 nickel.

TABLE 2.—*Thermal Expansion of Sample* 5542

(13 Per Cent Silicon, 0.76 Per Cent Iron, 0.15 Per Cent Copper)

Date	Coefficient of Expansion $\times 10^6$			Deviation from Bureau of Standards Determination		
	20°–100° C.	20°–200° C.	20°–300° C.	20°–100° C.	20°–200° C.	20°–300° C.
5/ 1/28	19.6	20.3	21.4	−0.1	+0.2	+0.1
7/13/28	19.6	20.4	21.5	−0.1	+0.3	+0.2
8/14/28	19.2	20.1	21.1	−0.5	0	−0.2
8/18/28	19.6	20.2	21.0	−0.1	+0.1	−0.3
9/25/28	19.5	20.2	21.2	+0.2	+0.1	−0.1
9/19/28	19.1	19.9	21.0	−0.6	−0.2	−0.3
10/15/28	19.1	20.0	21.1	−0.6	−0.1	−0.2
Bureau of Standards	19.7	20.1	21.3			

	20°–100° C.	20°–200° C.	20°–300° C.
Average all determinations	19.4	20.2	21.2
Maximum deviation from average, per cent	1.5	1.5	1.4
Average deviation from Bureau of Standards, per cent	±1.5	±0.5	±0.9
Maximum deviation of individual determinations from Bureau of Standards, per cent	3.1	1.5	1.4

specimen was used to check the apparatus from time to time, with the results tabulated in Table 2. These determinations indicate that the maximum probable error of any one determination should not be greater than 3 per cent in the temperature range 20° to 100° C. In the higher ranges of temperature, the probable error is not greater than 1.5 per cent.

TABLE 3.—*Thermal Expansion of Aluminum Alloys*

Sample No.	Composition by Analysis, Per Cent				Average Coefficient of Expansion per Deg. C. $\times 10^6$		
	Cu	Fe	Si	Ni	20°–100° C.	20°–200° C.	20°–300° C.
3544	2.47				22.8	23.6	24.2
5726	5.47	0.03	0.04		22.3	23.2	23.8
5727	10.				22.0	23.0	23.8
5728	20.				21.2	21.7	22.3
5791	33.20				19.7	20.2	20.8
5887	0.05	0.70	0.03		22.6	23.1	24.4
5896		4.45			20.4	22.3	23.3
5897		8.46			21.0	21.5	22.3
5878	0.035	0.06	4.71		21.8	22.4	23.5
5879	0.06	0.08	9.56		20.5	21.3	
5883	0.09	0.12	14.83		19.3	19.9	20.6
5884	0.10	0.16	19.70		18.5	18.7	19.0
8305			40.		14.7	16.0	17.1
5792	0.11	0.08	0.06	3.36	21.9	22.7	23.7
5504				7.49	20.5	21.7	22.9
5793	0.07	0.08	0.05	19.53	18.2	18.9	19.5
5727	9.86	0.03	0.04		22.0	23.0	23.8
5794	9.88	1.06	0.07		21.2	21.9	22.7
5795	9.77	5.04	0.06		19.9	20.8	21.5
5726	5.5	0.03	0.04		22.3	23.6	24.2
5600	5.14			5.00	21.3	22.0	22.8
5604	4.51			9.86	19.9	20.9	21.6
5605	9.78			5.04	20.5	21.5	22.2
5606	9.78	0.10	0.08	9.90	19.1	20.0	20.6
5792	0.11	0.08	0.06	3.36	21.9	22.7	23.7
5796	0.064	3.59	0.063	3.26	20.7	21.6	22.5
5797	0.036	8.45	0.084	3.09	19.5	20.3	21.2

Table 3 and Figs. 2 to 10 inclusive show the effect of some common alloying constituents on the thermal expansivity of pure aluminum.

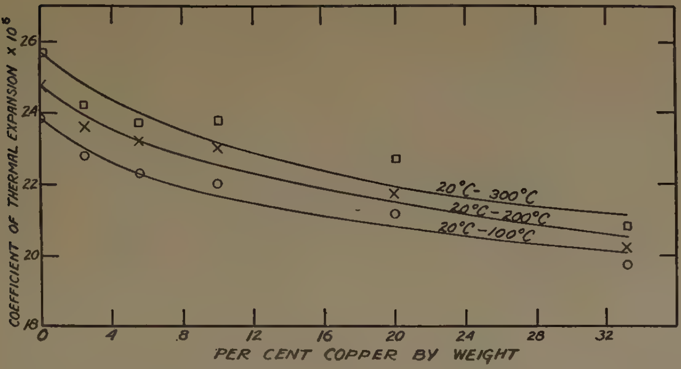

FIG. 2.—EFFECT OF COPPER ON THERMAL EXPANSIVITY OF ALUMINUM.

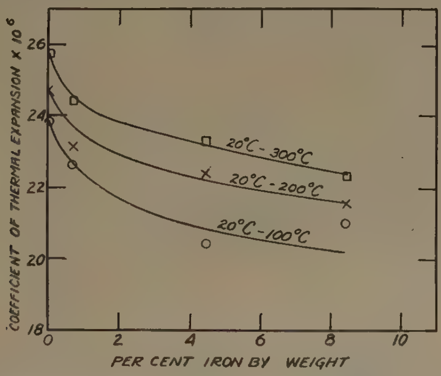

FIG. 3.—EFFECT OF IRON ON THERMAL EXPANSIVITY OF ALUMINUM.

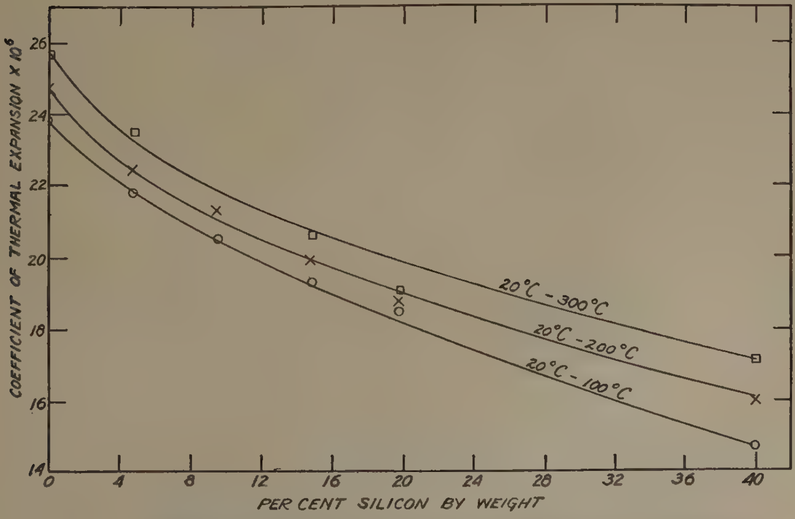

FIG. 4.—EFFECT OF SILICON ON THERMAL EXPANSIVITY OF ALUMINUM.

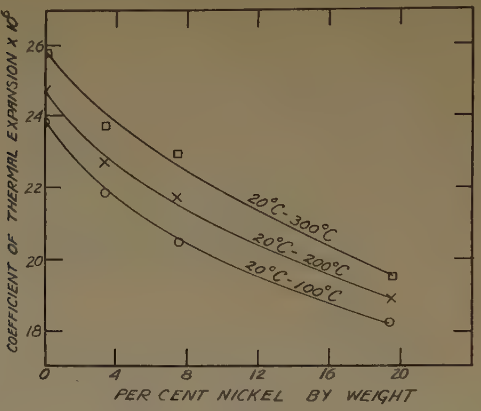

FIG. 5.—EFFECT OF NICKEL ON THERMAL EXPANSIVITY OF ALUMINUM.

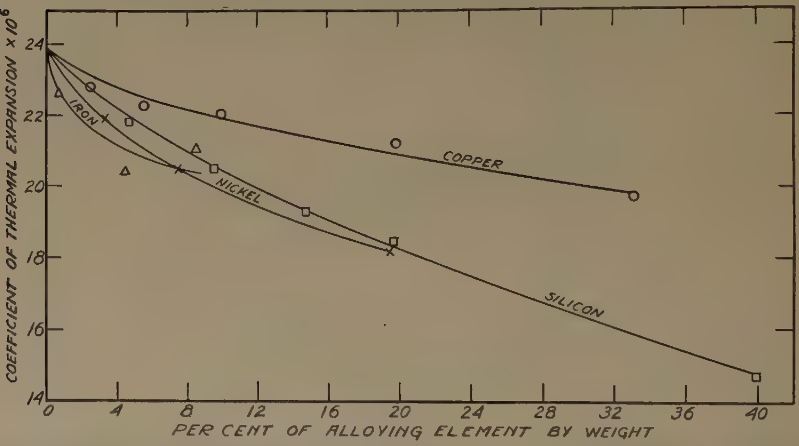

FIG. 6.—RELATIVE EFFECTS OF COPPER, IRON, SILICON AND NICKEL ON THERMAL EXPANSIVITY OF ALUMINUM.

Values plotted are average coefficients of expansion per degree Centigrade for the temperature interval 20° to 100° C.

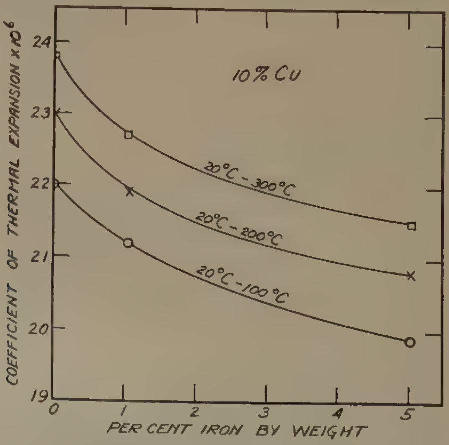

FIG. 7.—EFFECT OF IRON ON THERMAL EXPANSIVITY OF ALUMINUM ALLOY CONTAINING 10 PER CENT COPPER.

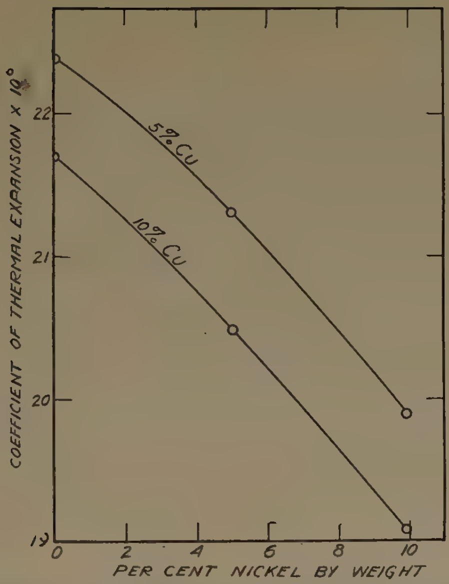

Fig. 8.—Effect of nickel on thermal expansivity of aluminum-copper alloys.

Values plotted are average coefficients of expansion per degree Centigrade for the temperature interval 20° to 100° C. Zero nickel values are estimated from the curves of Fig. 6.

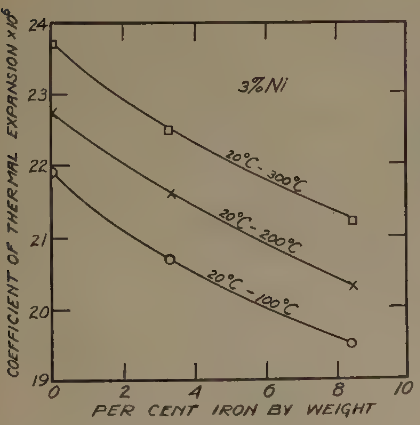

Fig. 9.

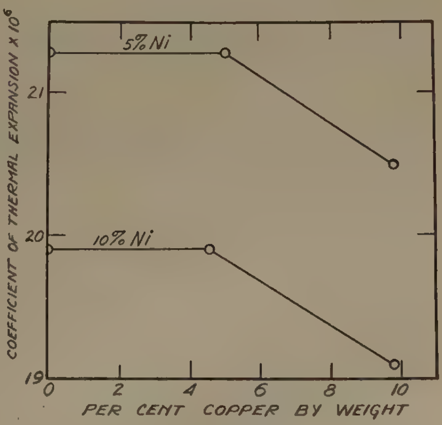

Fig. 10.

Fig. 9.—Effect of iron on thermal expansivity of an aluminum alloy containing 3 per cent nickel.

Zero iron values are estimated from the curves of Fig. 5.

Fig. 10.—Effect of copper on thermal expansivity of some aluminum-nickel alloys.

Values plotted are average coefficients of expansion per degree Centigrade for the temperature interval 20° to 100° C.

TABLE 4.—*Thermal Expansivity of Some Miscellaneous Aluminum Alloys*

Sample No.[a]	Composition, Per Cent									Average Coefficient of Expansion per Degree Centigrade × 10^6		
	Ca	Cr	Cu	Fe	Si	Ni	Mg	Mo	Mn	20°–100° C.	20°–200° C.	20°–300° C.
4200			4.03	0.82	13.35					19.8	20.6	21.4
4201			7.91	0.74	13.35					19.4	20.1	20.9
4202			4.05	0.78	13.22	4.12				18.5	18.9	19.8
4203			8.02	0.80	13.19	4.10				18.0	18.7	19.3
4205			4.13	0.80	12.68	4.44		1.36		18.2	18.9	19.6
4290			3.18	0.96	20.29				1.07	17.4	18.0	18.8
4284			3.14	0.84	19.30	4.18			1.08	16.6	17.0	17.8
4292			14.14	0.81	8.31					19.6	20.1	21.0
4297			9.78	0.42	10.23	3.91				18.8	19.1	20.2
5658			7.88	0.5[b]	0.3[b]	5.26	0.44			20.7	21.4	22.1
5599			2.08	0.5[b]	14.0	4.12	1.32			18.3	19.0	19.7
5506			0.02[b]	0.15[b]	0.1[b]	7.46	1.33			21.5	22.3	23.5
5503			0.02[b]	0.15[b]	0.1[b]		8.98			23.3	24.1	24.6
5507			0.00	0.18	0.10				3.66	20.7	22.2	23.1
5508	7.62		0.02[b]	0.15[b]	0.1[b]					20.3	21.0	21.7
5511		5.16	0.02[b]	0.15[b]	0.1[b]					20.7	21.9	23.0
5480			0.85	0.5[b]	13.51	1.93	0.99			19.0	20.2	21.0
5668			1.52	0.53	13.54	3.06	1.02			18.3	19.4	20.1
5100			7.04	0.84	6.78	7.18				19.3	19.8	20.9

[a] Determinations on samples 4200 to 4297 inclusive were made by Hidnert and Sweeney of the U. S. Bureau of Standards. Annealed 1 hr. at 400° C. and slowly cooled to room temperature; all other samples annealed 20 hr. at 225° C.

[b] Composition by mixture; all others by analysis.

Table 4 gives the expansivity of a number of complex alloys. The majority of determinations in this table were made at the Bureau of Standards; the remainder at the Aluminum Research Laboratories.

Table 5 gives the coefficients of thermal expansion of some commercial aluminum alloys. Some of these values are the result of direct measurements but the majority are estimated from the composition and the fundamental data available on the effect of composition on thermal expansivity. These estimations are probably more representative than an individual determination on a random specimen of commercial alloy. More practically reliable data could only be obtained from determinations on a number of specimens covering the range of chemical composition and fabricating practice for each alloy. A number of coefficients are given to 0.5 in the third significant figures; it is not felt that these estimations are correct to more than the second significant figure. However, there appeared to be justification for differentiating between the relative expansivities of some alloys whose coefficients would otherwise be recorded as identical.

Discussion of Results

The general effect of adding metals of lower thermal expansivity to aluminum is an alloy with a lower coefficient of expansion than pure aluminum. The coefficient of expansion generally decreases with increasing quantities of the alloying element when the coefficient of expansion of the latter is lower than that of pure aluminum. Of the elements copper, iron, silicon and nickel, iron is most efficacious in reducing the coefficient of expansion of aluminum. Nickel exerts the next largest effect. Silicon is almost as efficient as nickel, while copper is decidedly less effective than any of these three metals.

The results of present determinations on the various aluminum alloy series are somewhat at variance with the results reported by some of the other investigators. The variation is greatest in the aluminum-copper alloy system. Hidnert's curves indicate that copper exerts little effect on the thermal expansion of aluminum up to 4 per cent by weight. From 4 to 8 per cent copper, the coefficient of expansion increases and even becomes greater than that of pure aluminum. Above about 8 per cent copper, the coefficient of expansion appears to decrease at the lower temperatures but remains substantially constant at temperatures from 300° to 500° C. McCullough also reports some rather anomalous results in the aluminum-copper series, inasmuch as all his determinations for copper contents from about 2.3 to 7 per cent showed higher thermal expansion than pure aluminum.

The higher copper contents in McCullough's results indicate a decrease in coefficient of expansion with increase in copper content. It would appear that this should be the result to be expected upon the addition of

TABLE 5.—*Approximate Coefficients of Thermal Expansion of Some Commercial Aluminum Alloys*[a]

Trade Designation	Nominal Composition, Per Cent							Average Coefficients of Thermal Expansion per Deg. C. (to be multiplied by 10^{-6})					
	Cu	Fe	Si	Mg	Mn	Ni	Zn	20°–100° C.	68°–212° F.	20°–200° C.	68°–392° F.	20°–300° C.	68°–572° F.
Alcoa 2S	99 per cent Aluminum							24	13.3	25	13.8	26	14.4
Alcoa 3S					1.25			24	13.3	25	13.8	26	14.4
Alcoa 4S				1.0	1.25			24	13.3	25	13.8	26	14.4
Alcoa 14S	4.5			0.35	0.8			22	12.2	23.5	13.0	25	13.8
Alcoa 17S	4.0			0.5	0.5			22	12.2	23.5	13.0	25	13.8
Alcoa A17S	2.5			0.3				22.5	12.5	24	13.3	23.5	14.1
Alcoa B17S	3.5			0.3				22.5	12.5	24	13.3	25.5	14.1
Alcoa C17S	4.0		1.25	0.5				22	12.2	23.5	13.0	25	13.8
Alcoa 25S	4.5		0.8		0.8			22	12.2	23.5	13.0	25	13.8
Alcoa 32S	0.8		12.5	1.0		0.8	(0.1 Ti)	19.5	10.8	20.5	11.4	21.5	11.9
Alcoa 51S			1.0	0.6				23.5	13.0	24.5	13.6	25.5	14.1
Alcoa X56S				6.0				24	13.3	25	13.8	26	14.4
Alcoa 70S	1.0			0.4	0.8		9	24.5	13.6	26	14.4	27	15.0
Alcoa 12	8.0							22.5	12.5	23.5	13.0	24.5	13.6
Alcoa 43			5.0					22	12.2	23	12.7	24	13.3
Alcoa 47			12.5					20	11.1	20.5	11.3	21.5	11.9
Alcoa 100	99 per cent Aluminum							24	13.3	25	13.8	26	14.4
Alcoa A108	4.5		5.75					21.5	11.9	22.5	12.5	23	12.7
Alcoa 108	4.0		4.0					22	12.2	23	12.7	24	13.3
Alcoa 109	12.0							22	12.2	23	12.7	24	13.3
Alcoa 112	7.5	1.2					1.5	22	12.2	23	12.7	24	13.3
Alcoa 113	7.5	1.2	1.5				1.5	22	12.2	23	12.7	24	13.3
Alcoa 122	10.0	1.2		0.2				22	12.2	23	12.7	23.5	13.0
Alcoa A122-70	12.0			0.1				22	12.2	23	12.7	23.5	13.0
Alcoa 132	1.0	1.0	14.0	1.0		2.5		19	10.5	20	11.1	21	11.6
Alcoa 142	4.0			1.5		2.0		22.5	12.5	23.5	13.0	24.5	13.6
Alcoa 144	10.0		4.0	0.2				21.5	11.9	22.5	12.5	23	12.7
Alcoa 146	7.8			0.1			1.8	22	12.2	23	12.7	24	13.3
Alcoa 195-T4	4.0							23	12.7	24	13.3	25	13.8
Alcoa 195-T62	4.0							23	12.7	24	13.3	25	13.8
Alcoa 195-T6	4.0							23	12.7	24	13.3	25	13.8
Alcoa B195-T4	4.5		3.0					22	12.2	23	12.7	24	13.3

TABLE. 5.—(*Continued*).

Trade Designation	Nominal Composition, Per Cent							Average Coefficients of Thermal Expansions per Deg. C. (to be multiplied by 10^{-6})					
	Cu	Fe	Si	Mg	Mn	Ni	Zn	20°–100° C.	68°–212° F.	20°–200° C.	68°–392° F.	20°–300° C.	68°–572° F.
Alcoa D195-T4	5.5		0.7					23	12.7	24	13.3	25	13.8
Alcoa 196-T62	4.0			0.2				23	12.7	24	13.3	25	13.8
Alcoa 212	8.0	1.0	1.2					22	12.2	23	12.7	24	13.3
Alcoa 220				10.0				24.5	13.6	25.5	14.1	26.5	14.7
Alcoa 214				4.0				24	13.3	25	13.8	26	14.4
Alcoa 216				6.0				24	13.3	25	13.8	26	14.4
Alcoa 313	3.0		4.0					22	12.2	23	12.7	24	13.3
Alcoa 314	4.0		13.5					20	11.1	20.5	11.3	21.5	11.9
Alcoa 318	2.0		8.0					20.5	11.4	21.5	11.9	22.5	12.5
Alcoa A334	3.0		4.0	0.3				22	12.2	23	12.7	24	13.3
Alcoa A355	1.4		5.0	0.5	0.75	0.75		21.5	11.9	22.5	12.5	23.5	12.7
Alcoa 355	1.2		5.0	0.5				22	12.2	23	12.7	24	13.3
Alcoa 356			7.0	0.3				21.5	11.9	23	12.7	23.5	13.0
Alcoa 13			12.0					20	11.1	20.5	11.3	21.5	11.9
Alcoa 14	14.0		2.0					21	11.6	22	12.2	23	12.7
Alcoa 83	2.0		3.0					22.5	12.5	23.5	13.0	25	13.8
Alcoa 85	4.0		5.0					21	11.6	22	12.2	23	12.7
Alcoa 93	4.0		2.0			4.0		21	11.6	22	12.2	23	12.7

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[a] The majority of these coefficients are estimations and refer to the material in a stable condition as regards volume changes incidental to reheating to the neighborhood of 300° C. The coefficients in the Fahrenheit scale were derived from those in the Centigrade scale and no greater accuracy is implied by reason of their being given to three significant figures.

copper with a coefficient of expansion of about 0.000017 per degree Centigrade to aluminum with an expansion of about 0.000024 per degree Centigrade. The addition of copper brings about no change in type of atomic arrangement of the aluminum. Unless such change in atomic arrangement takes place, it is difficult to understand why the addition of copper should increase the expansivity of aluminum. It is suspected that these somewhat anomalous results may be ascribable to permanent changes in length of the specimens occurring during determination of the expansion coefficient. Hidnert records changes in length as great as 0.11 per cent. Very small permanent changes in the length of the specimen bring about correspondingly larger errors in the coefficients of expansion. The percentage errors for a permanent length change of 0.01 per cent for two coefficients of expansion for various temperature intervals follow:

Coefficient of Expansion per Deg. C.	Error for Temperature Intervals, Per Cent		
	20° to 100° C.	20° to 200° C.	20° to 300° C.
0.000016	8	3.5	2
0.000024	5	3	1

These permanent changes in length recorded by Hidnert, which probably have affected the determinations of some of the other investigators, are undoubtedly the result of changes in the relative proportions of phases present incidental to the heating for the expansion determination. It is known, for example, that precipitation of the compound $CuAl_2$ from a supersaturated solution in solid aluminum results in an increase in volume. The magnitude of such changes has been estimated in these laboratories by measuring the linear changes taking place when supersaturated solid solutions are reheated to various temperatures. A 6 per cent copper alloy quenched from 535° C. exhibited the unit linear changes listed in Table 6.

TABLE 6.—*Unit Linear Changes of* 6 *Per Cent Copper Alloy Quenched from* 535° *C.*

Temperature of Reheating, Deg. C.	Unit Permanent Changes in Length
500	0.00009
425	0.00029
375	0.00041
325	0.00050
275	0.00135
225	0.00151

The measurements from which these figures were taken were made at room temperature following quenching from the reheating temperature. The rate at which the alloy approaches equilibrium at any specified temperature of reheating varies in a regular manner, equilibrium being obtained much more rapidly at the high temperatures than at the low. Specimens were repeatedly reheated and measured until no further change took place.

The variation of the rate at which equilibrium is attained with temperature is illustrated by the fact that 240 hr. at 150° C. is required to bring about equilibrium in an alloy containing about 10 per cent copper and 0.2 per cent magnesium, whereas at 170° C. only 90 hr. were required, and at 225° C. no length changes could be noted after 3 hr. It should be recognized, of course, that the magnitude of these volume changes varies between alloy systems, and in any specific system with the degree of supersaturation. For example, the maximum unit linear expansion noted for alloys containing about 6 per cent copper quenched from a high-temperature solution treatment was about 0.0015. On the other hand, as cast in a chill mold with no subsequent solution heat treatment, aluminum-copper alloys containing upwards of about 4 per cent copper exhibit a maximum unit permanent expansion of about 0.0006 to 0.001. The permanent unit linear expansion for the saturated aluminum-silicon solid solution was found to be 0.0016, while the pure aluminum-magnesium silicide solid solution alloys showed no definite changes in volume on reheating following quenching from a solution treatment.

Thus, the total volume changes of aluminum alloys incidental to temperature changes may be due to at least two quite different factors. One of these has been termed "growth" or "permanent growth" and is a manifestation of the variation with temperature of the mutual solid solubilities of the various structural phases present. The change due to this factor may or may not be reversible, depending on the range of the temperature cycle and the rate of heating and cooling. In practical applications the magnitude of this effect varies considerably depending on the initial condition of the alloy. The maximum effect thus far observed corresponds to a unit linear change of about 0.0016.

A second factor effecting volume change with changes in temperature is the expansion of the atomic lattice or true thermal expansion. The volume changes attributable to this factor are perfectly reversible and are generally independent of the rate of heating or cooling.

In view of the fundamental difference between these two factors, it appears logical that each should be evaluated separately. Determinations of coefficients of thermal expansion made indiscriminately with regard to the structural condition of the alloy are not true coefficients of thermal expansion but algebraic summations of effects due to phase changes, internal stress relieval and thermal expansion. It would seem desirable that expansivity should be determined on material as nearly as possible free from potential "growth" and internal stress. It is believed that such data may be more accurately applied to practical problems than data, however precise, obtained on material in indefinite structural condition as regards volume changes.

The material used in this investigation, with the exception noted in Table 4, was stabilized by heating at 225° C. followed by air cooling to room temperature, for a length of time sufficient to bring about equilibrium as regards "growth." In most systems this requires about 20 hr. at temperature. Within the range of temperature investigated, 20° to 300° C., these volume changes in the systems investigated are for the most part irreversible.

SUMMARY

The coefficients of thermal expansion of a number of aluminum alloys have been determined with a probable error within about 3 per cent.

It is shown that structural changes attendant upon the reheating during the determination of thermal expansion may, if disregarded, bring about relatively large errors in the determination.

Approximate coefficients of thermal expansion for a number of commercial aluminum alloys have been estimated from the fundamental data available on the effect of various alloying elements on the thermal expansivity of pure aluminum.

ACKNOWLEDGMENTS

The author desires to express his indebtedness to Mr. R. S. Archer, under whose direction much of this work was carried out, and to Mr. J. H. Riendeau, who made many of the determinations.

DISCUSSION

(R. G. Waltenberg presiding)

H. H. Lester, Watertown, Mass. (written discussion).—The apparatus that Mr. Kempf used is similar in principle to one used at Watertown Arsenal, except that temperatures were measured differently. That is, the specimen was inclosed in a nickel chamber and the expansion of this cylinder relative to quartz was calibrated in terms of temperature, the nickel cylinder thus serving as a thermometer. The advantage of this is a more self-contained equipment and greater ease of taking readings. The temperatures are also somewhat more certain. There seems to be no loss of accuracy in temperature measurements. The apparatus is illustrated in Fig. 11.

D. F. McFarland, State College, Pa.—I was much interested in the permanent growth shown. It seems to be similar to the permanent growth that takes place in cast iron, which causes considerable trouble in some of the gray cast iron. The cause is probably different in the two cases. There has been a good deal of discussion as to what causes it in gray cast iron, such as graphite precipitation and changes in the condition of carbon. The results here also indicate that it is desirable to make not one determination on a new substance but to make the determination, then cool down and make it over again and see whether the results are the same. I had not suspected it could be found in other alloys than cast iron.

H. Scott, Pittsburgh, Pa. (written discussion).—Besides contributing some exceptionally valuable data, Mr. Kempf has pointed out the need for a special preparation technique for expansion test specimens. While the basic preparational requirements are clearly set forth, some amplification of this important subject may be appropriate.

With few exceptions the common metals and alloys as normally cooled contain impurities in supersaturated solid solution which precipitate on heating at a comparatively low temperature, producing an irreversible change in volume. If heated to a sufficiently high temperature, the precipitate will again dissolve and the original irreversible change is annulled. An expansion curve between these two temperature levels will, therefore, take the form of a hysteresis loop; hence the designation irreversible for the expansion anomaly causing the loop.

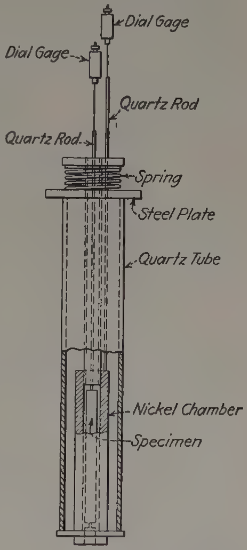

Fig. 11.—Apparatus used for measuring thermal expansion at Watertown Arsenal.

The usual purpose of the expansion test is to determine the reversible expansion alone in an unambiguous manner. This requires special annealing to eliminate so far as is necessary irreversible expansion effects. Since the rate of precipitation as well as distribution of solute changes rapidly with temperature, the specimen must be annealed at a temperature where nearly complete precipitation will occur in a time interval of the same magnitude as that of the test. Kempf's temperature of 225° C. held 20 hr. appears adequate for aluminum. It should be recognized, however, that for each metal, or perhaps each base metal in the case of alloys, a different temperature may be required. Also irreversible expansion becomes prominent again on heating much above that temperature, thereby limiting the temperature range over which reversible expansion can be measured reliably.

Another manner in which irreversible effects may be circumvented is by observing room-temperature length following quick cooling after each high-temperature observation. By so doing the irreversible expansion at each temperature is evaluated from which a correction can be applied to obtain the true reversible expansion. Such a procedure implies, of course, that expansivity does not change appreciably with variation in amount of solute dissolved. This assumption is justified by the fact that the effects of the solute on expansivity and its change in distribution with temperature is normally small.

Data on the effects of alloying elements in pure metals are scarce and Mr. Kempf has made a considerable addition to our information thereon. The interpretation of these data presents an interesting problem. To assist in that direction it would be desirable to have values of the maximum and minimum solid solubility of the elements concerned, particularly the latter. One might expect a discontinuity in the expansivity versus composition curves starting at the minimum solid solubility value for the element varied.

L. W. Kempf (written discussion).—Mr. McFarland calls attention to the similarity between aluminum alloys and cast iron as regards permanent growth. The permanent growth exhibited by aluminum alloys differs somewhat from that which takes place in cast iron. In aluminum alloys growth appears to be entirely the result of precipitation of intermetallic compounds from supersaturated solid solutions and the alloys may be easily and completely stabilized for any given temperature range, after which no further volume change takes place unless the temperature range of reheating is changed. The magnitude of the volume change in aluminum alloys is also much smaller than in gray cast iron. No such simple explanation seems to account adequately for the volume changes encountered in cast iron.

Dr. Scott correctly calls attention to the fact that the rate of precipitation and distribution of the solute change with temperature and with the nature of the systems. In the alloy systems investigated it was found that the period of time at 225° C. necessary for complete stabilization varied with the alloy system. In all cases, however, 20 hr. at 225° C. was found to be more than adequate to complete the volume changes.

Dr. Lester has described an interesting variation in the method of determining coefficient of thermal expansion by means of differential expansion. We found that the accurate measurement of relative linear motion was far more difficult than the establishment and determination of uniform thermal conditions. We therefore preferred to limit the measurements of linear motion to the differential expansion of quartz and the unknown specimen, and determine our temperatures electrically.

Equilibrium Relations in Aluminum-chromium Alloys of High Purity

By William L. Fink* and H. R. Freche,* New Kensington, Pa.

(New York Meeting, February, 1933)

This is the thirteenth paper of a series from the laboratories of the Aluminum Company of America presenting the results of investigations of equilibrium relations in aluminum-base alloys prepared from electrolytically refined aluminum. The ninth paper, on The Constitution of High-purity Aluminum-titanium Alloys,[1] presented a type of system that had not previously been encountered in aluminum alloys. Subsequent work has shown that there are several similar binary aluminum diagrams including that of aluminum and chromium. The present investigation was limited to the extreme aluminum end of the aluminum-chromium system.

The first systematic investigation of the aluminum-chromium equilibrium diagram was carried out by Hindrichs.[2] The resulting equilibrium diagram with some imaginary additions suggested by Guillet[3] is shown in Fig. 1.

Recently Gotō and Dōgane[4] investigated the constitution of aluminum alloys containing up to 32 per cent chromium, and presented the diagram that is reproduced in Fig. 2. Wide discrepancies in the two diagrams are evident.

The following intermetallic compounds have been reported in the literature: $AlCr$,[5,6] $Al_{10}Cr_{12}Si$,[5] $AlCr_4$,[6] $AlCr_3$,[7] Al_4Cr.[8]

Preparation of Alloys and Chemical Analyses

With the exception of sample Y4206, which will be described under Determination of Hyperperitectic Liquidus, the alloys were prepared from electrolytically refined aluminum[9] of which the analysis is given in

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* Aluminum Research Laboratories.

[1] W. L. Fink, K. R. Van Horn and P. M. Budge: *Trans.* A.I.M.E. (1931) **93,** Inst. Metals Div., 421.

[2] Hindrichs: *Ztsch. anorg. allg. Chem.* (1908) **59,** 430.

[3] *Rev. de Mét.* (1921) **18,** 682.

[4] *Proc.* World Eng. Cong., Tokyo (1929) **36, 31** Abs.

[5] Wöhler: *Lieb. Ann.* (1858) **106,** 118; *Idem* (1861) **115,** 102.

[6] L. Guillet: *Génie civil* (1902) **41,** 381.

[7] Reference of footnote 2.

[8] Reference of footnote 4.

[9] F. C. Frary: *Trans.* Amer. Electrochem. Soc. (1925) **47,** 275.

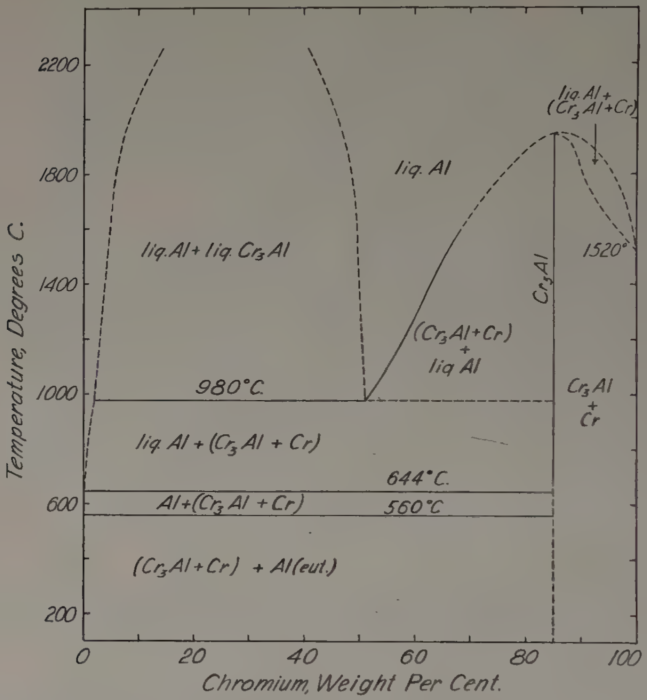

FIG. 1.—ALUMINUM-CHROMIUM CONSTITUTION DIAGRAM ACCORDING TO GUILLET.

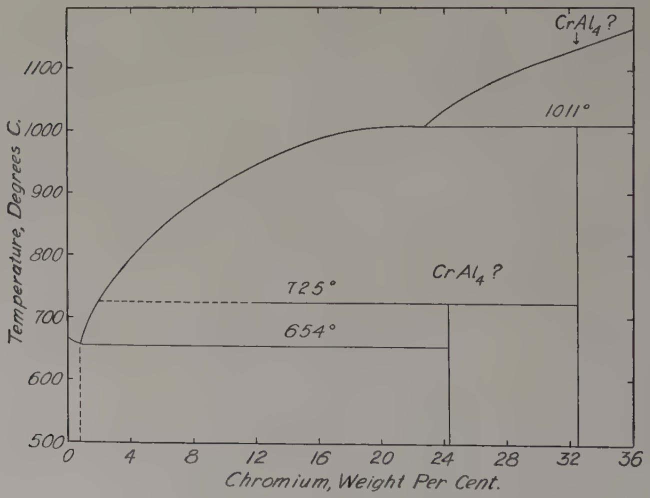

FIG. 2.—ALUMINUM-CHROMIUM CONSTITUTION DIAGRAM ACCORDING TO GOTŌ AND DŌGANE.

Table 1, and C.P. anhydrous chromic chloride. The reduction of $CrCl_3$ gave an alloy (Y5178) containing 1.41 per cent chromium, which was diluted with electrolytically refined aluminum to prepare alloys of lower chromium contents.

The chemical analyses were obtained on drillings from chill-cast plates 5 mm. thick, which were cast at a temperature considerably above the liquidus. The chromium was determined by the persulfate method.[10] The results of the analyses are given in Table 1.

TABLE 1.—*Chemical Composition of Alloys*

Description of Sample	Sample No.	Composition of Alloys, Per Cent			
		Cr	Fe	Si	Cu
Electrolytically refined aluminum			0.01	0.01	0.01
Chromium-rich alloys prepared from anhydrous $CrCl_3$.	Y5178	1.41	0.02	0.01	0.01
	Y5175	1.17	0.02	0.01	0.01
	S2647	1.50	0.01	0.01	0.01
Prepared from Sample Y5178 and electrolytically refined aluminum.	Y6104	0.01			
	Y6105	0.02			
	Y6106	0.03			
	Y6107	0.06			
	Y6108	0.10			
	Y5888	0.17			
	Y6109	0.21			
	Y8022	0.38			
	Y8387	0.46			
	Y8388	0.51			
	Y8389	0.58			
	Y6161	0.65			
	Y7405	1.03			
Prepared from Sample Y4206	Y5078	2.00			

MICROSCOPIC EXAMINATION OF CHILL-CAST SPECIMENS

A preliminary microscopic examination of a chill-cast specimen[11] (Y5175) containing 1.17 per cent chromium revealed the structure shown in Fig. 3. This structure is similar to that sometimes observed in aluminum-titanium, and aluminum-manganese alloys. The unetched needles of primary constituent were gray when illuminated by the light from a carbon arc filtered through a 78A Wratten filter. The etching characterististies of the constituent are listed on the next page.

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[10] Standard Methods of Analysis, Aluminum Company of America.

[11] The casting technique employed was previously described by Dix and Keith: Equilibrium Relations in Aluminum-manganese Alloys of High Purity. *Proc.* Inst. Met. Div., A.I.M.E. (1927) 315.

ETCHING SOLUTION	EFFECT ON CONSTITUENT
0.5 per cent hydrofluoric acid	Constituent outlined
1 per cent sodium carbonate solution (cold)	Constituent not attacked
1 per cent sodium carbonate solution (70° C.)	Constituent turns irridescent brown
1 c.c. hydrofluoric + 1.5 c.c. hydrochloric + 2.5 c.c. nitric acid + 95 c.c. water[12]	Like 0.5 per cent hydrofluoric acid
25 per cent nitric acid (70° C.)	No effect
20 per cent sulfuric acid (70° C.)	No effect
10 per cent sodium hydroxide solution	Darkens constituent
10 per cent sodium hydroxide + 1 per cent sodium carbonate solution	Darkens constituent

COMPOSITION OF CONSTITUENT OCCURRING IN ALUMINUM-RICH ALLOYS

The aluminum-chromium constituent was separated chemically by dissolving away the aluminum matrix of furnace-cooled sample Y5178.

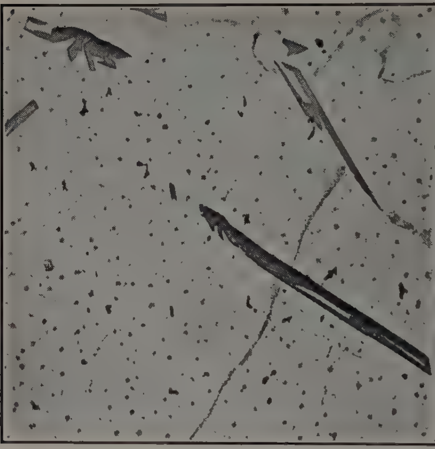

FIG. 3.

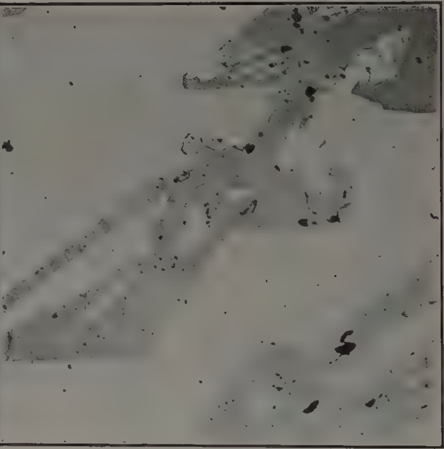

FIG. 4.

FIG. 3.—1.17 PER CENT CHROMIUM ALLOY (Y5175-2226). × 500. Specimen was chill-cast. Etched with 10 per cent NaOH + 1 per cent Na_2CO_3.

FIG. 4.—1.03 PER CENT CHROMIUM ALLOY (7405-A-1915). × 500. Specimen was slowly solidified in furnace. Unetched. The area illustrated was taken near the bottom of the ingot.

The bottom of the ingot that contained large crystals, as shown in Fig. 4, was treated with dilute hydrochloric acid. The acid first dissolved the parts of the matrix that were midway between particles of constituent. The pits so formed gradually increased in size until only the plates of constituent remained unattacked. Fig. 5 is a picture of a portion of the sample after partial decomposition. Large clean plates with smooth idiomorphic surfaces were selected from the final residue under a binocular microscope. No metallic aluminum could be detected by X-ray diffrac-

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[12] Dix and Keller: *Min. & Met.* (1928) **9**, 327.

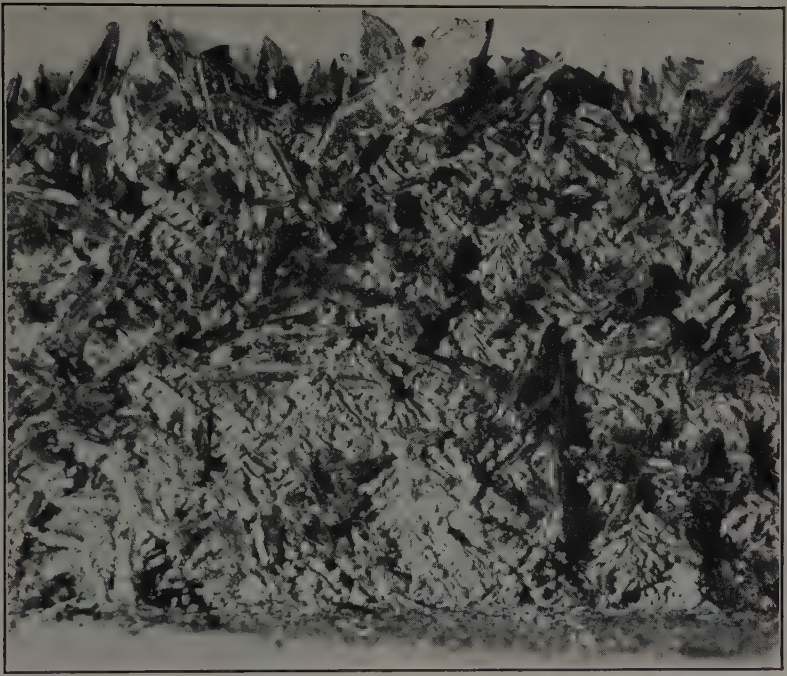

FIG. 5.—1.03 PER CENT CHROMIUM ALLOY (Y7405-A-1903). × 2. BOTTOM OF INGOT HAVING STRUCTURE SHOWN IN FIG. 4.

Part of sample has been dissolved in dilute hydrochloric acid leaving $CrAl_7$ plates standing in relief.

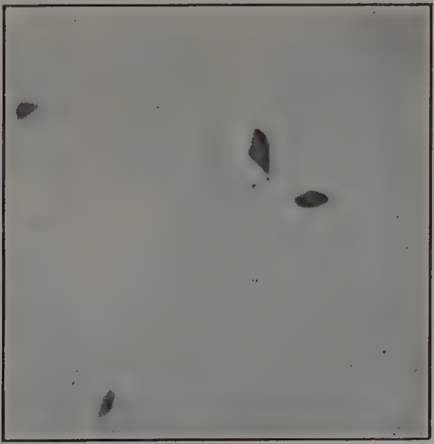

FIG. 6.—0.65 PER CENT CHROMIUM ALLOY (Y6161-A-1898D). × 1000.

Specimen heated 72 hr. at 630° C. Unetched. Shows the rhombohedral particles of $CrAl_7$.

tion methods. Chemical analysis of these crystals corresponded to the formula $CrAl_7$.

THERMAL ANALYSIS

Cooling curves were taken of alloys up to 2 per cent chromium. A sample of about 200 grams in a graphite crucible was heated in a small electric furnace to a temperature well above the liquidus and cooled at a rate of 4° C. per minute. The temperatures were read by means of a Leeds & Northrup precision potentiometer (type K) and a platinum, platinum-rhodium thermocouple with an iced cold-junction. The couple was carefully calibrated against the freezing point of electrolytically refined aluminum and was protected from the melt according to the practice recommended by the U. S. Bureau of Standards.[13] The results of the thermal analyses are given in Table 2.

TABLE 2.—*Thermal Arrests of Aluminum-chromium Alloys*

Sample No.	Percentage of Chromium	Liquidus Arrest	Peritectic Arrest
6107	0.06	659.9	
6108	0.10	660.0	
5888	0.17	660.3	
6109	0.21	660.5	
6161	0.65	695	660.7
7405	1.03	735	660.9
5078	2.00	780	661.0

The cooling curve of sample Y6161 (0.65 per cent chromium) is shown in Fig. 7. It will be noted that after the peritectic temperature has been reached the temperature remains constant for a time, then rapidly decreases a few tenths of a degree, and finally remains almost constant until solidification is complete. A solidus temperature lower than the peritectic temperature can be explained by a departure from true equilibrium conditions.[14]

DETERMINATION OF HYPERPERITECTIC LIQUIDUS

Although the primary arrests on the cooling curves of the chromium alloys are more definite and reproducible than those at the aluminum end of many other binary aluminum systems, it seemed desirable to check the hyperperitectic liquidus by the more accurate method[15] of analyzing the melt in equilibrium with the precipitated crystals of $CrAl_7$. A 500-gram charge of a high-purity sample (S2647) containing 1.50 per cent chromium was used for this purpose. The alloy was heated in a small alundum-lined plumbago crucible to 900° C., slowly cooled to 728° C. and maintained at that temperature for 2 hr. After removing the dross from the surface of the melt, a sample for chemical analysis was taken with a small ladle preheated to the temperature of the melt. After another 15 min. at the same temperature, a duplicate sample was taken. The sample was chill-cast in a graphite mold. The temperature was slowly decreased to 695° C., held at that temperature 2 hr., and an analysis sample taken as before. A duplicate sample was taken after an additional 25 min. Table 3 gives the compositions of the samples taken.

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[13] U. S. Bur. Stds. *Tech. Paper* 170 (1921) 193.

[14] See the discussion of Constitution of High-purity Aluminum-titanium Alloys. *Trans.* A.I.M.E. (1931) **93,** Inst. Metals Div., 421.

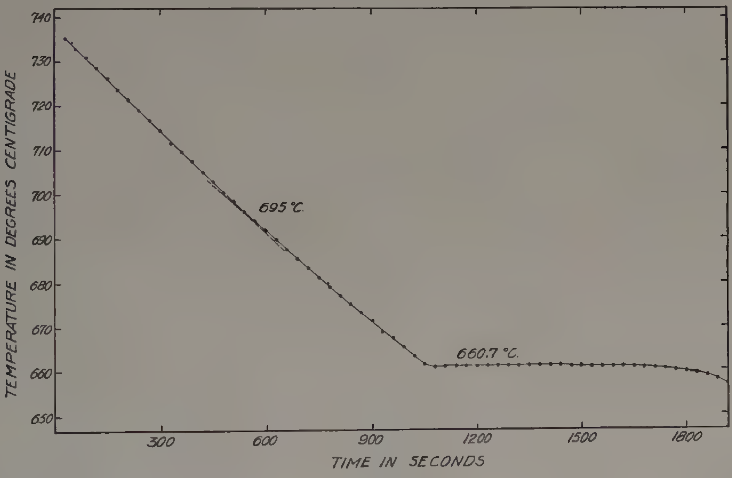

FIG. 7.—TYPICAL COOLING CURVE FOR AN ALLOY CONTAINING 0.65 PER CENT CHROMIUM.

A similar experiment was carried out using a 7-kg. charge of sample Y4206, which was prepared by adding metallic chromium to electrolytically refined aluminum. The composition of this sample was 9.94 per cent chromium, 0.19 per cent iron, 0.02 per cent silicon, 0.01 per cent copper. The larger volume of metal made it easier to obtain a sample free from crystals of $CrAl_7$. The high percentage of iron was not as objectionable as would at first appear because the first crystals to precipitate carried some of the iron. Only 0.07 per cent iron remained in the melt when the first sample was taken. The results of this experiment are listed in Table 4.

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[15] H. J. Miller: The Penetration of Brass by Tin and Solder with a Few Notes on Copper-tin Equilibrium Diagram. *Jnl.* Inst. Metals (1927) **37**, 188.

W. L. Fink, K. R. Van Horn and P. M. Budge: Constitution of High-purity Aluminum-titanium Alloys. *Trans.* A.I.M.E. (1931) **93**, Inst. Metals Div., 421.

W. L. Fink and H. R. Freche: Equilibrium Relations in Aluminum-cobalt Alloys of High Purity. *Trans.* A.I.M.E. (1932) **99**, 141.

TABLE 3.—*Solubility of* $CrAl_7$ *in Molten Aluminum Containing* 0.01 *Per Cent Iron*

Sample No.	Temperature, Deg. C.	Chromium, Weight Per Cent
S2630	728	0.95
S2631	728	0.94
S2748	695	0.66
S2749	693	0.64

TABLE 4.—*Solubility of* $CrAl_7$ *in Molten Aluminum Containing* 0.07 *Per Cent Iron*

Sample No.	Temperature, Deg., C.	Chromium, Weight Per Cent
Y5112	790	2.07
Y5113	785	1.96
Y5114	770	1.60
Y5115	770	1.59
Y5116	753	1.34
Y5117	753	1.38
Y5118	730	1.00
Y5119	730	1.00
Y5120	702	0.75
Y5121	702	0.75
Y5122	685	0.56
Y5123	685	0.57

COMPOSITION OF MELT AT PERITECTIC TEMPERATURE

In the experiments described in the preceding section it was impossible to obtain samples below 675° C. that were entirely free from crystals. Consequently the composition of the liquid in equilibrium with the solid at the peritectic temperature was determined by extrapolating the hyperperitectic liquidus according to an empirical formula. The composition so determined is 0.41 weight per cent chromium.

SOLID SOLUBILITY OF CHROMIUM IN ALUMINUM

Since equilibrium can be attained much more quickly in cold-rolled sheet than in cast specimens, the solubility specimens were prepared in the following way: One-pound ingots (2 by 9 by 10 cm.) were chill-cast in a graphite mold, hot-rolled to 2-gage (6.5 mm.) and then cold-rolled to 20-gage (0.8 mm.) sheet.

Microscopic examination of specimens of this sheet which had been heated at 530° C. for various periods of time showed that equilibrium

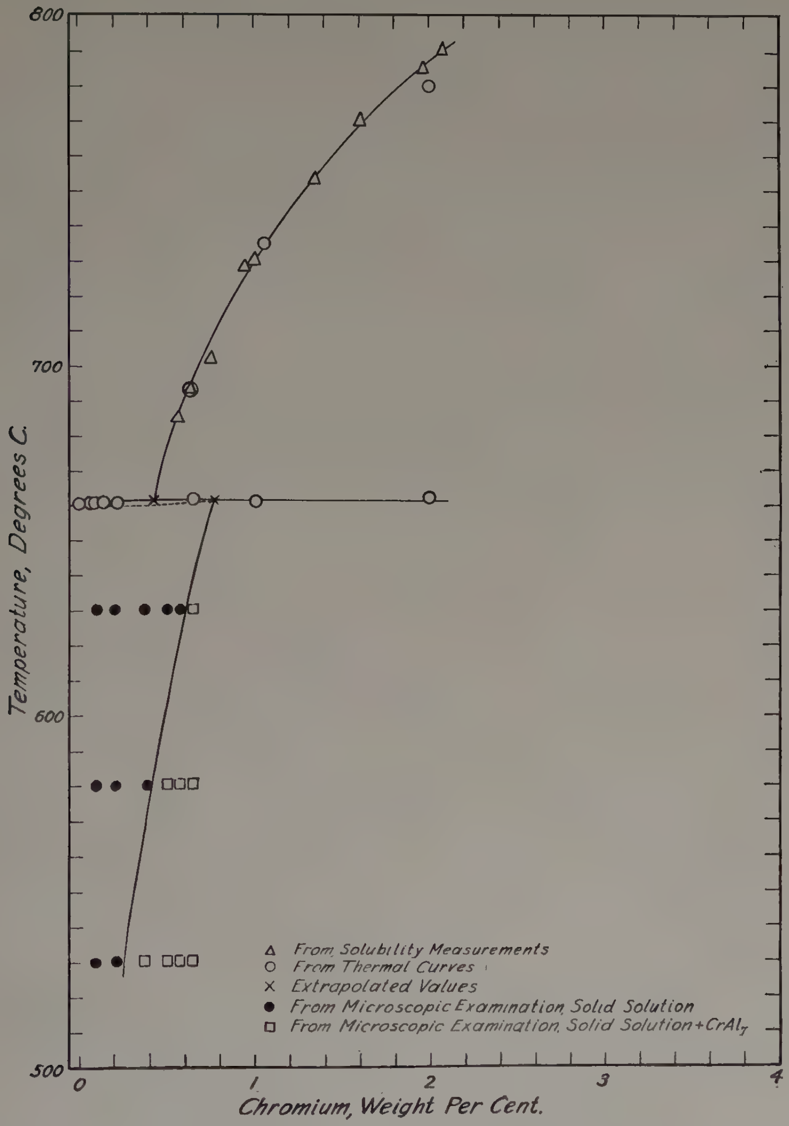

Fig. 8.—Aluminum end of aluminum-chromium diagram.

was established in less than 72 hr. Therefore a separate set of cold-rolled specimens was annealed for 72 hr. at each of the three temperatures investigated (530°, 580° and 630° C.). The solid solubility of chromium in aluminum was determined by microscopic examination of the quenched specimens. The results are shown in Fig. 8.

An extrapolation of the solubility curve to 661° C. gives 0.77 per cent as the solid solubility of chromium in aluminum at the peritectic temperature.

Fig. 6 shows particles of $CrAl_7$ out of solution in the 0.65 per cent chromium sample which had been annealed at 630° C.

Aluminum End of Aluminum-chromium Diagram

The aluminum-chromium diagram from 0 to 2 per cent chromium is represented in Fig. 8. The hypoperitectic solidus, which was not determined experimentally, is shown as a straight dotted line drawn from the melting point of aluminum to the solid solubility limit at 661° C. (the peritectic temperature).

Acknowledgment

The authors acknowledge with thanks the assistance of Dr. K. R. Van Horn, who verified the homogeneity of the separated crystals by X-ray methods; Mr. C. J. Walton, who polished some of the specimens for microscopic examination, and Mr. H. V. Churchill, under whose direction the chemical analyses were made.

Equilibrium Relations in Aluminum-manganese Alloys of High Purity, II*

By E. H. Dix, Jr.,† William L. Fink† and L. A. Willey,† New Kensington, Pa.

(New York Meeting, February, 1933)

The results of a preliminary investigation of the aluminum-iron-manganese system showed that small amounts of iron (0.10 per cent) substantially reduce the solid solubility of manganese in aluminum. This is clearly shown in the photomicrographs of three alloys, Figs. 1 to 3. Fig. 1, of an alloy containing 1.04 per cent manganese after a heat treatment at 626° C. for 45 hr., shows only solid solution. This alloy contained less than 0.008 per cent iron. Fig. 2 shows the abundance of a constituent (which undoubtedly contains aluminum, manganese and iron) in an alloy containing 1.00 per cent manganese and 0.11 per cent iron after a solution heat treatment at 625° C. for 63 hr. For comparison, Fig. 3 is included to show the relatively small amount of constituent ($FeAl_3$) in a similarly heat-treated aluminum alloy containing 0.10 per cent iron but no manganese.

These data necessitated a reconsideration of the binary aluminum-manganese diagram that was previously presented,[1] inasmuch as the alloys used in that work contained from 0.02 to 0.05 per cent iron.

This paper is the fourteenth of a series from the Research Laboratories of the Aluminum Company of America reporting the results of investigations of equilibrium relations in aluminum-base alloys of high purity. The purpose was to determine the phase relations in aluminum with aluminum-manganese alloys containing the smallest amount of iron that could be realized with the purest material available at the present time (less than 0.01 per cent iron).

Since the previous publication from these laboratories, five investigations of the aluminum-manganese system have been reported. Krings and Ostmann[2] assigned the formula $MnAl_4$ to the compound at the aluminum end of the system, and found a eutectic between this compound and aluminum at 649° C. and 3 per cent manganese.

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* Part I was published in *Proc.* Inst. Metals Div., A.I.M.E. (1927).

† Aluminum Research Laboratories.

[1] E. H. Dix, Jr. and W. D. Keith: Equilibrium Relations in Aluminum-manganese Alloys of High Purity. *Proc.* Inst. Metals Div., A.I.M.E. (1927) 315.

[2] W. Krings and W. Ostmann: Beitrag zur Kenntnis des Dreistoffsystems Kupfer-Aluminium-Mangan und seiner Magnetischen Eigenschaften. *Ztsch. anorg. Chem.* (1927) 145.

Rassow[3] investigated the aluminum-manganese alloys containing from 0 to 40 per cent manganese. The results of that investigation are

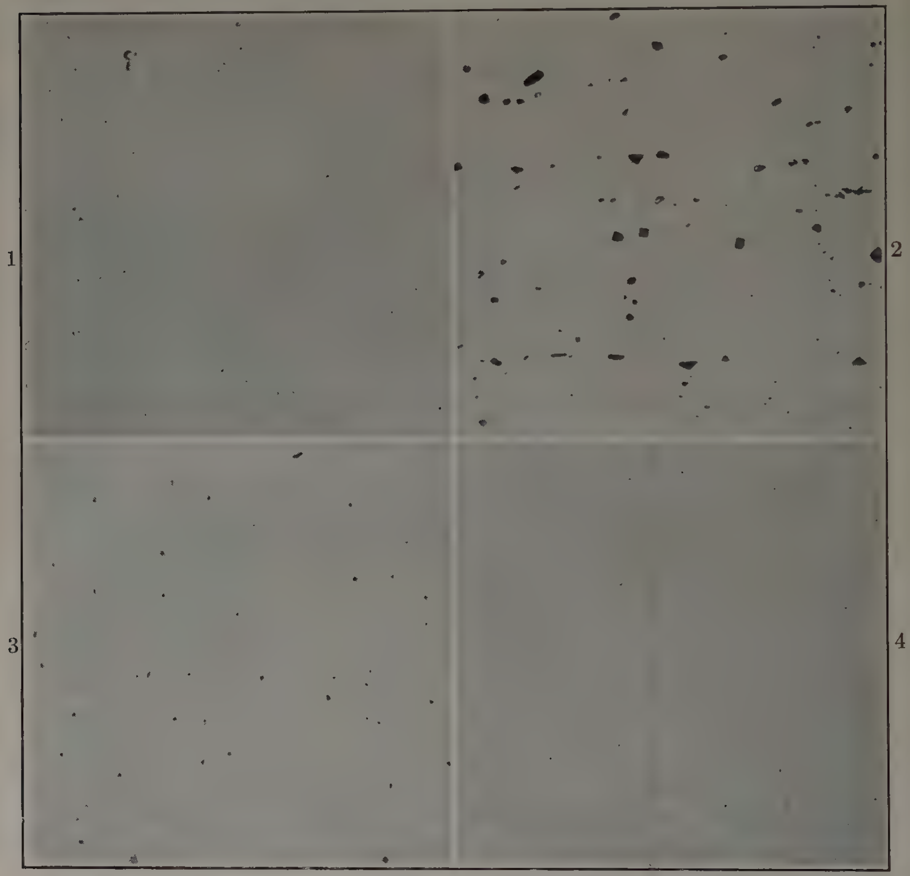

Fig. 1.—1.04 per cent manganese alloy (Y8956-Y6565M1-A3755D). × 500.
Specimen heat-treated 45 hr. at 626° C. and quenched. Shows only solid solution. Etched with 0.5 per cent HF.

Fig. 2.—1.00 per cent manganese, 0.11 per cent iron alloy (S1833-S1168-2-A3779D). × 500.
Specimen heat-treated 63 hr. at 625° C. and quenched. Shows large amount of constituent containing aluminum, manganese and iron. Etched with 0.5 per cent HF.

Fig. 3.—0.10 per cent iron alloy (S1161-A3745D). × 500.
Specimen heat-treated 63 hr. at 625° C. and quenched. Shows small particles of FeAl$_3$. Etched with 0.5 per cent HF.

Fig. 4.—1.01 per cent manganese, 0.09 per cent silicon alloy (S4448-A3782D). × 500.
Specimen heat-treated 63 hr. at 625° C. and quenched. Shows only solid solution. Etched with 0.5 per cent HF.

summarized by the diagram of Fig. 5. The eutectic is shown at 650° C. and 2.2 per cent manganese. There are indicated two isothermal phase changes, one at 670° C. and the other at 820° C. The former is interpreted as a polymorphic transformation of $MnAl_7$ and the latter as a peritectic reaction between $MnAl_3$ and the melt to form $MnAl_7$. Rassow did not investigate the eutectic concentration or the solid solubility but accepted the results obtained by Dix and Keith.

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[3] Von E. Rassow: Die Konstitution der Aluminiumreichen Aluminium-Mangan-Legierungen. *Hauszeitschrift* (1929) VI, 187–190.

Ishiwara[4] has investigated the entire binary aluminum-manganese system with the exception of the limits of solid solution at the aluminum end. His diagram, Fig. 6, differs from that shown by Rassow in that it does not show a peritectic reaction at 820° C. or the existence of $MnAl_7$. Moreover, the phase change occurring at 670° C. was explained as a peritectic reaction between the compound $MnAl_3$ and the melt, forming the compound $MnAl_5$.

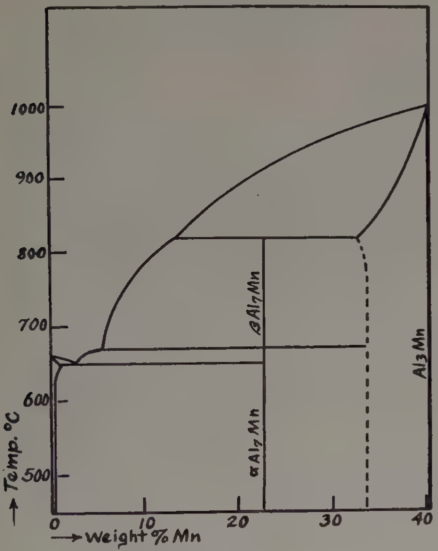

Fig. 5.

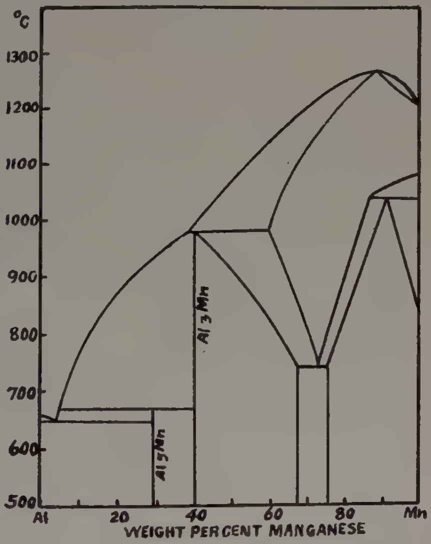

Fig. 6.

Fig. 5.—Diagram of aluminum-manganese system from 0 to 40 per cent manganese. (*Rassow.*)

Fig. 6.—Equilibrium diagram of the aluminum-manganese system. (*Torajiro Ishiwara.*)

Bradley and Jones[5] made X-ray diffraction patterns of some annealed aluminum-manganese alloys. From the patterns, they concluded that the compounds $MnAl_7$ and $MnAl_3$ occurred at the aluminum end of the system below 600° C.

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[4] T. Ishiwara: Equilibrium Diagrams of the Aluminum-manganese, Copper-manganese and Iron-manganese Systems. Tohoku Imp. Univ. *Sci. Repts.* (1930) **19,** 501.

[5] A. J. Bradley and Phyllis Jones: The Aluminum-manganese System of Alloys. *Phil. Mag.* (1931) **12,** 1137.

Bosshard[6] determined the solid solubility of manganese in aluminum by an electrical conductivity method. Although he found lower solubility values at all temperatures below approximately 640° C. than those previously reported from these laboratories, the difference may be attributed to the relatively large amount of iron present in his alloys (0.3 per cent). Bosshard stated that "Silicon in particular may bring about a modification of the results since it enters into the formation of a silicide, MnSi . . . " However, the authors find that silicon does not have as pronounced an influence as iron. Fig. 4 shows that 0.09 per cent silicon did not cause any precipitation in a 1 per cent manganese alloy, whereas 0.1 per cent iron produced the precipitation shown in Fig. 2.

MATERIALS USED

Electrolytically refined aluminum[7] of the highest purity obtainable was used throughout the investigation. The chemical analyses showed the following impurities: 0.003 to 0.005 per cent silicon, 0.006 to 0.008 per cent iron, and 0.003 to 0.004 per cent copper.

For the preparation of alloys containing more than 92 per cent aluminum, the manganese was obtained by the reduction of Baker's analyzed C.P. manganous chloride (containing 0.002 per cent iron) with aluminum. For the alloys containing less aluminum, metallic manganese of the following composition was used: 1.63 per cent silicon, 1.24 per cent iron, 0.12 per cent copper, 0.85 per cent aluminum, 96.16 per cent manganese by difference.

Preparation of Alloys.—For the production of the high-purity aluminum-manganese alloys, several manganese-rich alloys were first prepared by the addition of anhydrous manganous chloride to aluminum. This method of producing aluminum-manganese alloys was first employed by Wöhler[8] in 1860. The alloys containing smaller amounts of manganese were prepared by adding the required amount of hardener to high-purity aluminum at 700° to 750° C.

The manganous chloride was dried, first at 100° C. and then at gradually increasing temperatures up to about 500° C. The anhydrous chloride was finely powdered and gradually added to high-purity aluminum at 800° to 900° C. A recovery of from 60 to 75 per cent of the manganese was realized in the alloys prepared in this manner. The following is a typical analysis of these alloys or hardeners: 0.01 per cent silicon, 0.01 per cent iron, 0.01 per cent copper and 6.23 per cent manganese.

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[6] Bosshard: Study of Binary Alloys of Aluminum and Manganese Containing from 0.05 to 3.5 per cent of Manganese. Report No. 231, Bureau International de L'Aluminium, 1932.

[7] F. C. Frary: Electrolytic Refining of Aluminum. *Trans.* Amer. Electrochem. Soc. (1925) **47**, 275.

[8] Wöhler: *Lieb. Ann.* (1860) **115**, 102.

For the preparation of sheet specimens used in the solubility determinations, ingots (2 by 9 by 10 cm.) were cast in a graphite mold. For thermal analysis, cylinders (4 cm. in diameter by 6 cm. long) were cast in a graphite mold. The samples for chemical analysis were chill-cast in the form of slabs 5 mm. thick.

Chemical Analysis.—All of the alloys were analyzed for manganese by the persulfate-arsenite method.[9] The results of the analyses are given in the preceding paragraphs and in Table 1.

TABLE 1.—*Analysis of Alloys*

Alloy No.	Kind of Hardener Used	Weight Percentage			
		Si	Fe	Cu	Mn
Y6558	Prepared from $MnCl_2$	0.003	0.006	0.003	0.05
Y6559					0.10
Y6560					0.21
Y6561					0.32
Y6562					0.42
Y6563					0.62
Y6564					0.82
Y6565					1.04
Y6566		0.016	0.008	0.003	1.55
Y6567					2.06
Y6568					2.49
Y9777		0.01	0.01	0.01	0.52
Y9760					1.01
Y9804					1.55
Y9526					2.03
Y9430		0.01	0.01	0.01	4.00
S1049		0.02	0.01	0.01	6.10
S357		0.01	0.01	0.01	6.23
S5321	Metallic Mn				9.9
S2439–1		0.17	0.12	0.01	10.0
S4699					19.4
S3241					22.7
S3242					25.3
S3243					28.6
S5340					29.8
S5253–1		0.54	0.42	0.06	32.0
S5359					36.4

THERMAL ANALYSES

The thermal analyses were made on the cylindrical samples previously described. The samples were melted in a straight-wall graphite crucible 4 cm. inside diameter and 10 cm. in depth, provided with a graphite cover. To protect the thermocouple from the corrosive action of the melt, a protection tube 5 mm. outside diameter and 2 mm. inside diameter was prepared from a high-grade alundum cement. A 22-gage chromel-alumel thermocouple was used in connection with a Leeds & Northrup precision potentiometer. To assure accuracy, the thermocouple was calibrated against the freezing point of high-purity aluminum before and after the analysis of each alloy.

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[9] Standard Methods of Analysis, Aluminum Company of America.

The temperature of the thermal arrests on both heating and cooling are given in Table 2.

Inasmuch as the cooling curves give low values for the liquidus on account of undercooling, the primary arrests were not used in the construction of the equilibrium diagram. It will also be noted that cooling and heating curves give different temperatures for arrest No. 5. Since undercooling is more probable than overheating, the temperature of 710° C. should be given more weight. Additional experimental evidence favoring the higher temperature is described below.

TABLE 2.—*Thermal Analysis*

Alloy No.	Mn, Per Cent	Cooling Curve Arrests						Heating Curve Arrests					
		1 Liquidus	2	3	4	5	6 Eutectic	1 Liquidus	2	3	4	5	6 Eutectic
Y9777[a]	0.52	659.6						659.6					
Y9760[a]	1.01	659.2						659.2					
Y9804[a]	1.55	658.8						658.8					
Y9526[a]	2.03						658.4						658.4
Y9430[a]	4.00						658.5						658.5
S1049[a]	6.10					678.3	658.4					710.2	658.5
S5321	9.9	785.0				678.0	657.0	806.0				710.0	657.0
S4699	19.4	871.0			823.0	680.0	655.0	887.0			Not detected	704.0	655.0
S5340	29.8	946.0	918.0	Not detected	835.0	678.0		945.0	916.0	879.0	836.0	705.0	
S5359	36.4	991.0	932.0	874.0	829.0			991.0	932.0	908.0	Not detected		

[a] High-purity alloys.

THE HYPEREUTECTIC LIQUIDUS

The nature of aluminum-manganese alloys is such that the method used in determining the solubility curves for aqueous systems may also be used in determining the hypereutectic liquidus for this system. The method has been previously applied to the copper-tin system by Miller[10] and to various aluminum binary systems in the other investigations of this series.

The procedure may be briefly described as follows: Approximately 2¼ kg. of a high-purity aluminum-manganese alloy containing 6.23

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[10] H. J. Miller: The Penetration of Brass by Tin and Solder With a Few Notes on the Copper-tin Equilibrium Diagram. *Jnl.* Inst. Metals (1927) **37,** 188.

per cent manganese was heated to about 850° C. in a No. 10 plumbago crucible lined with alundum cement. An electric crucible furnace controlled with a Wilson-Maeulen controller was used. By placing a protected thermocouple just beneath the surface of the metal and connecting it with a Leeds & Northrup type K potentiometer a close check on the temperature of the melt was obtained. The metal was heated to 850° C. to insure complete solution of the constituent, then cooled to about 750° C. and held for approximately one hour. During this period the temperature of the melt did not vary more than ±2° C. When equilibrium had been obtained in this manner, the dross was carefully removed from the surface of the metal and a preheated ladle was filled with the clean surface liquid. The sample so taken was immediately chill-cast in the form of a slab 5 mm. thick, for chemical analysis. The temperature was decreased about 10° C. and a second sample was obtained after following the same procedure. This was continued until samples were obtained at several temperatures between 750° C. and the eutectic temperature. After the last sample had been obtained in this manner, the metal was very slowly cooled until complete solidification had taken place. A sample was cut from the center of the surface to obtain an approximation of the eutectic composition.

Much difficulty was experienced in obtaining samples of the liquid at temperatures immediately above 710° C. The crystals formed in this range did not settle readily. However, in the neighborhood of 710° C. a reaction took place and below that temperature the newly formed crystals settled to the bottom of the crucible, leaving a liquid layer at the top. It was found necessary to disregard the results on samples obtained in the first determination at temperatures above 710° C. because crystals were unavoidably included in the samples.

The difficulty was largely overcome by repeating the determination of the liquidus with a larger volume of metal. Approximately 11 kg. of an alloy (S2439-1) containing 10.0 per cent manganese was prepared from high-purity aluminum and metallic manganese. The alloy was prepared from metallic manganese on account of the difficulty of preparing such a large volume of 10 per cent alloy from the chloride. The results obtained indicate that the impurities introduced with the manganese had no substantial effect on this proportion of the diagram.

Before any samples were taken the transformation occurring at about 710° C. was investigated. The alloy was completely melted and then slowly cooled to about 715° C. At this temperature the alloy *appeared* to be almost completely solidified. A graphite stirring rod could not be forced into the metal. As the gradual cooling was continued, the proportion of the liquid phase *appeared* to increase. At about 700° C. the top third of the metal was entirely liquid while the crystals had settled to the bottom of the crucible. These crystals did not adhere or grow together enough to prevent forcing a stirring rod to the bottom of the crucible. On reheating to 715° C. the metal in the lower part of the crucible *appeared* to solidify again so that it could not be penetrated with the stirring rod. The liquid phase at the top, being low in manganese, remained unchanged.

The anomalous behavior of these alloys, that is, apparent solidification upon heating above 710° C., probably is caused by the peculiar crystal formation of the solid phase. Fig. 13 shows the lower surface of a 10 per cent manganese ingot which was heated at 720° to 730° C. for 2½ hr. and quenched. It is evident that the primary crystals have grown as interpenetrating aigrettelike clusters. Moreover, the crystals forming the clusters are usually hollow, like the one shown in Fig. 14. Obviously such a system of hollow crystalline members distributed throughout the liquid phase might possess considerable compressive strength, and give the erroneous impression that solidification was almost complete.

To determine the solubility at temperatures above 710° C. the alloy was diluted so as to contain about 6 per cent manganese. The same procedure was followed as in the first determination, except that occasionally during the period at constant temperature the crystals were forced toward the bottom of the crucible by pressing down with a preheated stirring rod. In this way it was possible to obtain satisfactory samples from a 6 per cent manganese alloy between 740° and 720° C.

The results of the two determinations are given in Table 3.

TABLE 3.—*Solubility of Manganese in Molten Aluminum*

Alloy No.	Temperature of Equilibrium, Deg. C.	Manganese, Per Cent
S2439-2	740	5.78
	731	5.26
	720	4.62
S357	699	3.44
	686	2.90
	675	2.51
	668	2.26
	(Sample from the surface of the solidified ingot 658.5° C.)	1.95

The results indicated two branches of the liquidus curve with slightly different slope intersecting at 710° C. The temperature of this discontinuity in the liquidus as well as the change in the character of the crystals confirms the reaction temperature determined by heating curves (710° C.).

SOLID SOLUBILITY

The solid solubility was determined by both electrical conductivity and microscopic methods. The specimens 0.64 by 19 by 500 mm. were cut from 22-gage sheet, which had been rolled in the following manner from the ingots previously described. The ingots were given a precautionary heating at 600° C. for 17 hr. to assist in homogenizing the structure. They were then rolled to 2-gage (6.5-mm.) sheet, annealed at 600° C. for 22 hr. to further homogenize the material, and cold-rolled to 22-gage (0.64-mm.) sheet.

Solution heat treatment was carried out within a closed aluminum block (10 cm. inside diameter by 20 cm. outside diameter by 53 cm. in length) placed in a Homo furnace. The temperature gradient and variation within this block were less than ±1° C.

The electrical conductivity determinations were made on all specimens within a short time after quenching from each solution heat treatment. These determinations were made by comparing the drop in potential across a known length of the specimens to that across a 0.001-ohm standard resistance connected in series. The drop in potential was measured with a Leeds & Northrup type K potentiometer while the specimens were kept at constant temperature (25° C.) in a thermostatically controlled oil bath. Specimens were given the consecutive heat treatments listed in Table 4.

TABLE 4.—*Consecutive Heat Treatments*

Specimens Marked Y6558M1 to Y6568M1			Specimens Y6558M2 to Y6568M2		
Hours	At Temp., Deg. C.	Quench	Hours	At Temp., Deg. C.	Quench
45	626	Cold water	89	500	Cold water
46	570	Cold water	47	500	Cold water
64	570	Cold water	17	625	Cold water
89	500	Cold water			

The results of the determinations by the electrical conductivity method indicated a solid solubility of 1.35, 0.78 and 0.36 per cent manganese at 626°, 570° and 500° C., respectively. Microscopic examination of the specimens verified the above results. Fig. 7 shows a photomicrograph of the first alloy (1.55 per cent Mn) in the series, to show particles of constituent out of solution after heat treatment at 626° C. An alloy containing 1 per cent, after the same heat treatment, showed only solid solution. (See Fig. 1.) A photomicrograph of an alloy containing 0.42 per cent manganese is shown in Fig. 8. This alloy was heat-treated at 500° C. and lies just above the limit of solid solubility at that temperature. Small particles of the manganese constituent are present.

Precipitation from Supersaturated Solid Solution.—The precipitation of the aluminum-manganese compound from supersaturated aluminum-rich solid solution presents interesting data which can be applied to the study of equilibrium conditions in other alloy systems. Fig. 9 shows the conductivity-concentration curve for specimens Y6558M1 to Y6568M1 quenched from 626° C. Fig. 10 shows the curve (I) obtained from the same specimens after the entire series of heat treatments previously described, and for comparison, a curve (II) obtained from specimens Y6558M2 to Y6568M2 heat-treated for 89 hr. at 500° C. without previous heat treatment. The difference between the two curves can be accounted for only by the fact that the first set of specimens had been heat-treated at higher temperatures prior to the final 500° C. treatment, whereas the second set of samples was still in the cold-rolled condition when it was placed in the furnace. The failure to attain equilibrium shown by curve I can be attributed in part to the absence of nuclei in the samples that consisted entirely of solid solution prior to the final heat treatment, since there is a greater degree of precipitation in the samples that contained particles of manganese constituent.

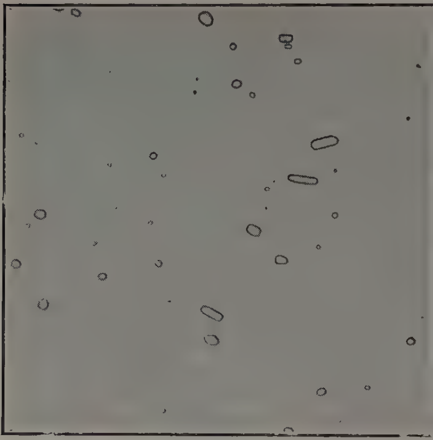

Fig. 7.

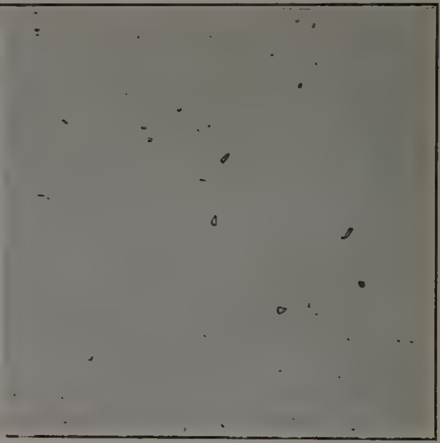

Fig. 8.

Fig. 7.—1.55 per cent manganese alloy (Y8956-Y6566M1-A3705D). × 500. Specimen heat-treated 45 hr. at 626° C. and quenched. Shows particles of $MnAl_6$ in a solid solution matrix. Etched with 0.5 per cent HF.

Fig. 8.—0.42 per cent manganese alloy (Y9591-Y6562M2-A3692D). × 500. Specimen heat-treated 136 hr. at 500° C. and quenched. Shows small particles of $MnAl_6$ after the above heat treatment. Etched 0.5 per cent HF.

This explanation is further strengthened by the microstructures of the specimens. Fig. 11 is a photomicrograph of an alloy containing 0.82 per cent manganese, which was given a solution heat treatment at 500° C. for 136 hr. directly from the cold-rolled condition. Copious precipitation has occurred throughout the grain. A specimen from the same sheet, but which had received heat treatment at 626° and 570° C. prior to the final heat treatment at 500° C. for 89 hr., had the structure illustrated in Fig.

12. No precipitation has occurred within the grains, though some has occurred at the grain boundaries.

The attainment of equilibrium was verified by reheat treatments at the same temperature, and by heating at 626° C. for 17 hr. a series of specimens which had previously been brought to equilibrium at 500° C.

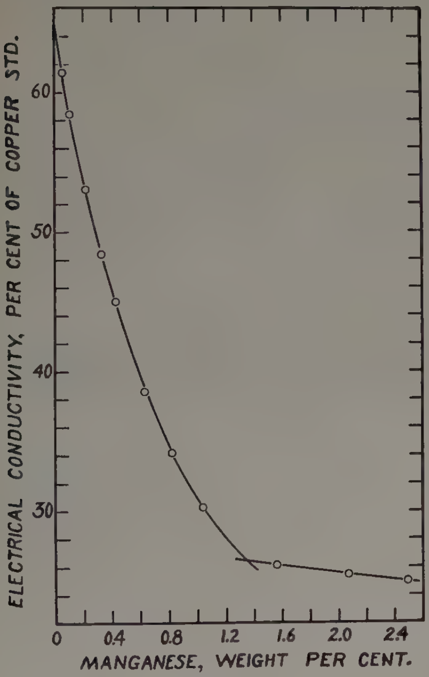

FIG. 9.

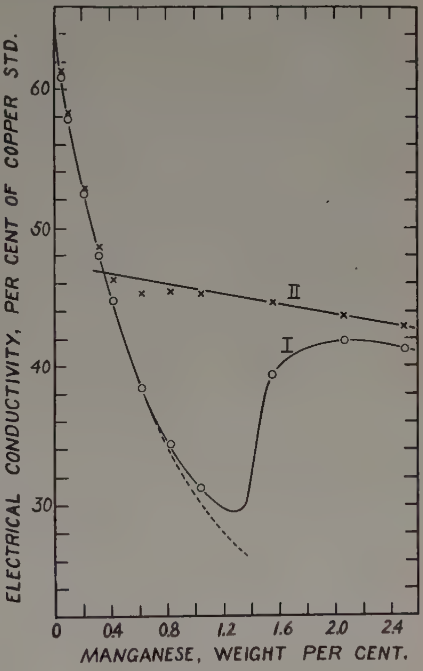

FIG. 10.

FIG. 9.—CONDUCTIVITY-CONCENTRATION CURVE.
Aluminum-manganese alloys heat-treated 45 hr. at 626° C. and quenched.

FIG. 10.—CONDUCTIVITY-CONCENTRATION CURVES.
I. Aluminum-manganese alloys heat-treated 45 hr. at 626° C., 110 hr. at 570° C. and 89 hr. at 500° C. Specimens quenched in cold water after each heat treatment. II. Aluminum-manganese alloys (cold-rolled 90 per cent) heat-treated 89 hr. at 500° C. and quenched.

In both cases identical conductivity-concentration curves were obtained at the given temperature.

INTERMETALLIC COMPOUNDS OCCURRING IN ALUMINUM-RICH ALUMINUM-MANGANESE ALLOYS

The compositions of the compounds occurring up to 10 per cent manganese have been studied. The composition of the compound at the extreme aluminum end of the diagram was first determined by separation and analysis of the constituent from an approximately 3 per cent high-purity alloy. The sample was melted, cooled slowly to 660° C., held for 30 min. at 660° to 665° C., and furnace-cooled.

Microscopic examination revealed only one phase in addition to the aluminum solid solution, as shown in Fig. 15. Most of the primary particles had settled to the bottom of the ingot which was used for the electrolytic separation of the constituent. The method used was the same as that previously described,[11] except that a 3 per cent hydrochloric acid solution was used. Clean, well formed crystals were selected from the residue under a binocular microscope and used for chemical and X-ray analyses. The analyses from two different separations gave 25.7 and 25.9 per cent manganese. This corresponds closely to the composition of $MnAl_6$ (25.35 per cent manganese). X-ray diffraction patterns of these crystals revealed only one phase.

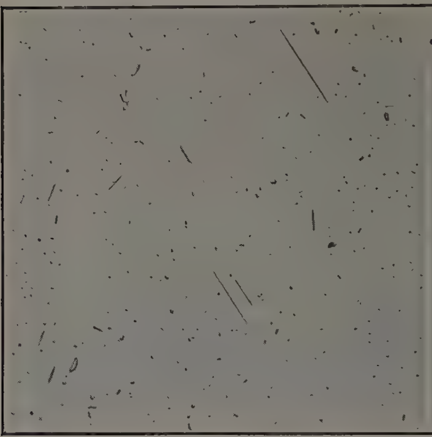

FIG. 11.

FIG. 12.

FIG. 11.—0.82 PER CENT MANGANESE ALLOY (Y9591-Y6564M2-A3693D). × 500. Specimen (cold-rolled 90 per cent) heat-treated 136 hr. at 500° C. and quenched. Shows an abundance of precipitation throughout the specimen. Etched with 0.5 per cent HF.

FIG. 12.—0.82 PER CENT MANGANESE ALLOY (Y9737-Y6564M1-A3694D). × 500. Specimen heat-treated 45 hr. at 626° C., 110 hr. at 570° C. and 89 hr. at 500° C. Shows precipitation at grain boundaries only. Etched with 0.5 per cent HF.

Since the formulas $MnAl_5$ and $MnAl_7$ had both been proposed for this constituent, alloys corresponding to these compositions were compared with an alloy corresponding closely with the formula $MnAl_6$. These samples were heated at 690° C. for 120 hr. and quenched. The resulting structures are shown in Figs. 16 to 18. Obviously the only sample approaching a single phase is that corresponding to $MnAl_6$. Even in this sample there are small particles of a second phase. This may be caused by atoms of the impurities replacing atoms of manganese in the compound $MnAl_6$, thereby producing the same effect as adding too much manganese. X-ray diffraction patterns confirmed the microscopic observations, and definitely identified the light phase in Fig. 16 as aluminum, and the dark phase in Fig. 18 as identical to the constituent shown in Fig. 14.

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[11] W. L. Fink and K. R. Van Horn: Constituents of Aluminum-iron-silicon Alloys. *Trans.* A.I.M.E. (1931) **93**, Inst. Met. Div., 383.

It would be expected that the crystals shown in Fig. 14, which form above the peritectic reaction at 710° C., would differ from $MnAl_6$ in composition as well as crystal structure. The specimen illustrated in Fig. 18 consisted of approximately equal quantities of $MnAl_6$ and the compound in question. It was therefore suspected that the composition of the dark phase might correspond to the formula $MnAl_4$.

In order to determine whether or not the compound is $MnAl_4$, the same methods were used as in the investigation of $MnAl_6$. Crystals electrolytically separated from the ingot illustrated in Figs. 13 and 14 were found to contain 32.3 per cent manganese. Alloys containing 32.0 and 36.4 per cent manganese by analysis were prepared and heat-treated at 755° to 765° C. for approximately 20 hr. The resulting structures are shown in Figs. 19 and 20. The structure shown in Fig. 19 would indicate that the manganese content of this alloy slightly exceeds that of the compound. However, the impurities (0.42 Fe, 0.54 Si, 0.06 Cu) would probably have the same proportional effect as was found in the case of $MnAl_6$. Making allowance for this effect, it seems probable that the formula of the compound is $MnAl_4$. X-ray diffraction patterns showed that the alloy ($MnAl_4$) shown in Fig. 19 is identical to the dark phase of Fig. 18 and the constituent of Fig. 14.

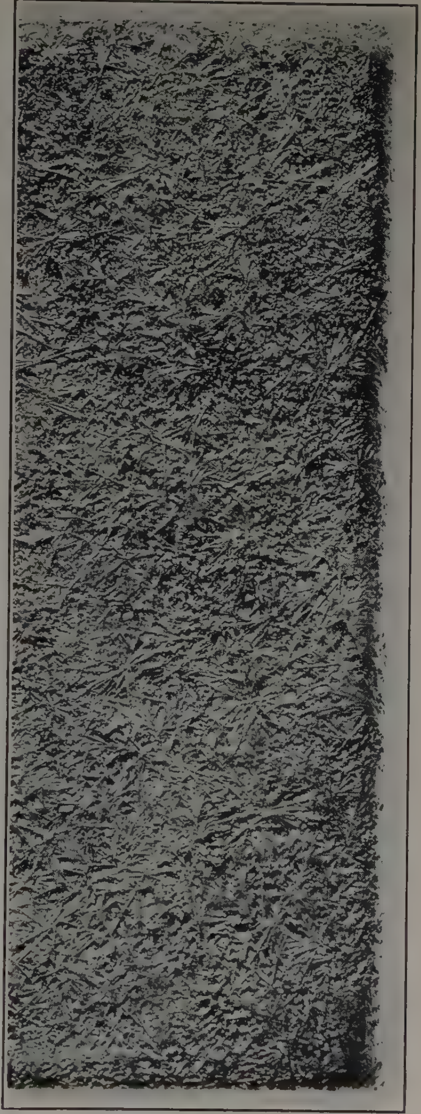
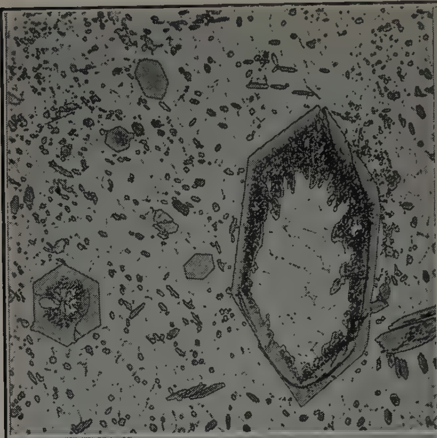


FIG. 13.—10.0 PER CENT MANGANESE ALLOY (S2439-1-S2988-A3214A). × 2.
Ingot prepared by slowly cooling the melt to 720° C., holding at 720° to 730° C. for 2½ hr. and quenching in cold water. Shows cluster formation of needlelike crystals ($MnAl_4$), standing in relief on unpolished and unetched bottom surface.

The composition of the next compound in the system, which appears as a dark phase in Fig. 20, has not been determined. It may be the compound $MnAl_3$ which has been frequently reported in the literature.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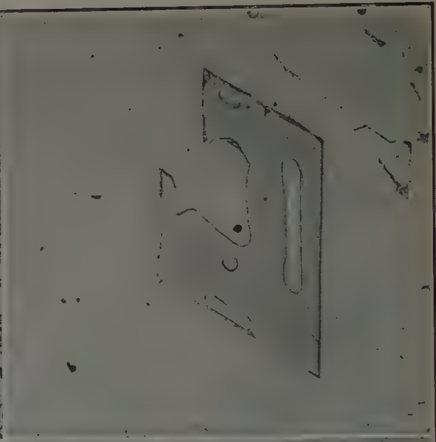
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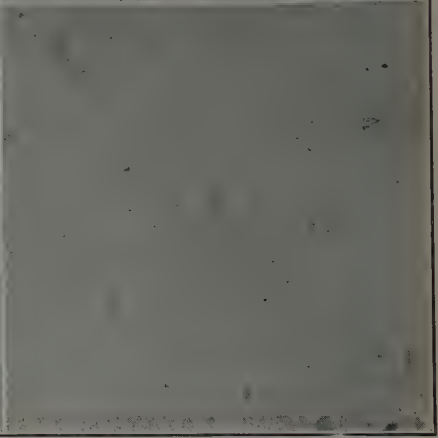
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Fig. 14.—10.0 per cent manganese alloy (S2988-A3780D). × 100.
Specimen from ingot shown in Fig. 13. Shows cross-sections of needles of intermetallic compound $MnAl_4$. Etched with 0.5 per cent HF.

Fig. 15.—Approximately 3.0 per cent manganese alloy (S2589-A3774). × 100.
Specimen from the bottom of an ingot prepared by slowly cooling the melt to 660° C., holding at 660° to 665° C. for 30 min., and slowly cooling till solidified. Shows primary crystal of the intermetallic compound $MnAl_6$. Etched with 0.5 per cent HF.

Fig. 16.—22.7 per cent manganese alloy (S3241-A3681D). × 500. An alloy corresponding to the formula $MnAl_7$.
Specimen heat-treated 120 hr. at 690° C. and quenched. Shows two phases; the aluminum manganese eutectic and the compound $MnAl_6$. Etched with 10 per cent NaOH-5 per cent H_2O_2.

Fig. 17.—25.3 per cent manganese alloy (S3242-A3683D). × 500. An alloy corresponding to the formula $MnAl_6$.
Specimen heat-treated 120 hr. at 690° C. and quenched. Shows the compound $MnAl_6$ with a small amount of $MnAl_4$. Etched with 10 per cent NaOH-5 per cent H_2O_2.

Under the microscope the compounds $MnAl_6$ and $MnAl_4$ in the unetched condition have very nearly the same color—a flat gray. Dilute sodium hydroxide solutions etch the two compounds in a somewhat

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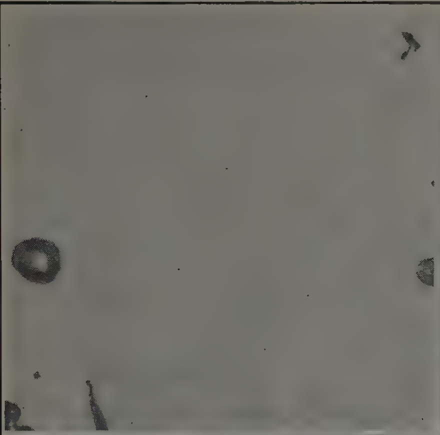

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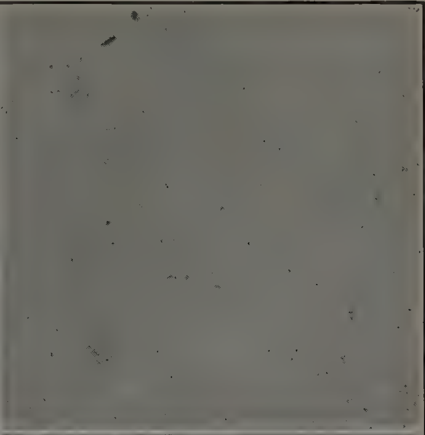
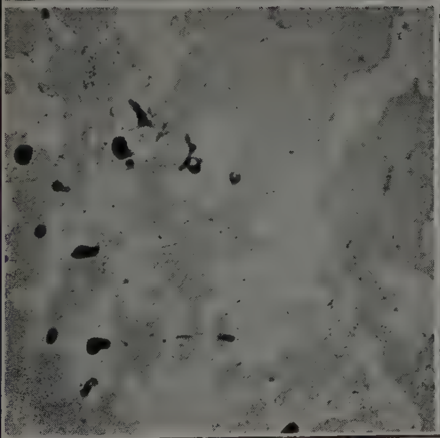


20



21

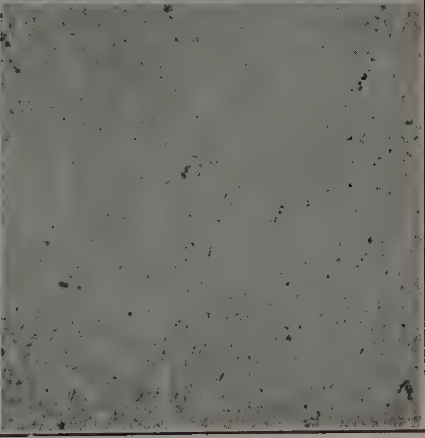


Fig. 18.—28.6 per cent manganese alloy (S3243-A3684D). × 500. An alloy corresponding to the formula $MnAl_5$.

Specimen heat-treated 120 hr. at 690° C. and quenched. Shows approximately equal amounts of $MnAl_6$ (light colored areas) and $MnAl_4$ (dark areas). Etched with 10 per cent NaOH-5 per cent H_2O_2.

Fig. 19.—32.0 per cent manganese alloy (0.54 per cent silicon, 0.42 per cent iron and 0.06 per cent copper) (S5253-1-A3952). × 500. An alloy having approximately the formula $MnAl_4$.

Specimen heat-treated approximately 20 hr. at 755° to 765° C. and quenched. Shows the compound $MnAl_4$ and a small amount of a second phase that may be $MnAl_3$. Etched with 10 per cent NaOH-5 per cent H_2O_2.

Fig. 20.—36.4 per cent manganese alloy (S5359-1-A3921D). × 500.

Specimen heat-treated approximately 20 hr. at 755° to 765° C. and quenched. Shows $MnAl_4$ (light areas) and a second phase that may be the compound $MnAl_3$. Etched with 10 per cent NaOH-5 per cent H_2O_2.

Fig. 21.—25.3 per cent manganese alloy (S3242D-A3805D). × 500.

Specimen heat-treated 64 hr. at 760° to 775° C. and quenched. Shows the compounds $MnAl_4$ and an aluminum-rich phase. Etched with 10 per cent NaOH-5 per cent H_2O_2.

different manner, and thus help in distinguishing between them. When the compounds occur in an aluminum matrix, a one per cent solution of NaOH etches $MnAl_6$ blue gray in 10 sec., whereas it etches $MnAl_4$ brown in the same length of time. Concentrated NaOH solution (e.g., 10 per cent) etches both compounds dark brown to black. Other etching solutions which are commonly used for aluminum alloys[12] (0.5 per cent hydrofluoric acid, 20 per cent sulfuric acid, and 25 per cent nitric acid) do not affect either compound appreciably. Although the one per cent sodium hydroxide solution is satisfactory for aluminum-rich alloys, it badly stains alloys which are so high in manganese that little or no aluminum phase is present. For such alloys a solution containing 10 per cent sodium hydroxide and 5 per cent hydrogen peroxide is preferable.

Aluminum End of Aluminum-manganese Equilibrium Diagram

The equilibrium diagram of the aluminum-rich aluminum-manganese alloys as determined in this investigation is shown in Fig. 22. In view of the pronounced effect of small quantities of iron on the solid solubility curve, this line may still differ appreciably from that of the true binary diagram, although the alloys all contained less than 0.01 per cent iron. If alloys spectroscopically free from iron had been used a still higher solid solubility might have been obtained. With the purity attained in this work the solid solubility decreases from about 1.82 per cent manganese at the eutectic temperature to 0.36 per cent manganese at 500° C.

In placing the eutectic horizontal at 658.5° C., the results from alloys containing 0.01 per cent iron were used and the lower temperatures indicated by the lower purity alloys, disregarded.

The hypoeutectic liquidus, as determined by cooling curves of alloys containing 0.01 per cent iron or less, is a straight line intersecting the eutectic horizontal slightly below 2 per cent manganese.

The lowest branch of the hypereutectic liquidus determined by measuring the solubility of $MnAl_6$ in high-purity aluminum intersects the eutectic horizontal at 1.95 per cent manganese and intersects the second branch of the liquidus at 710° C. and 4.06 per cent manganese. The second branch of the liquidus rises from this point to approximately 800° C. and 10 per cent manganese, and somewhat further. The exact point of intersection with the third branch of the liquidus has not been determined.

The peritectic reaction has been located at 710° C. by observation of the anomalous crystallization occurring at that temperature, by the discontinuity in the liquidus curve, and by heating curves. This temperature is consistent with the microstructures of samples having the composition $MnAl_6$ which were heat-treated at 690° and 725° C. At 690° C. $MnAl_6$ is stable, as shown in Fig. 17. At 725° C. a peritectic reaction has taken place and a heterogeneous structure obtains. This structure is similar to that of the same alloy heated at 760° to 775° C., illustrated in Fig. 21.

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[12] E. H. Dix, Jr. and W. D. Keith: Etching Characteristics of Constituents in Commercial Aluminum Alloys. *Proc.* Amer. Soc. Test. Mat. (1926) **26,** Pt. II, 317.

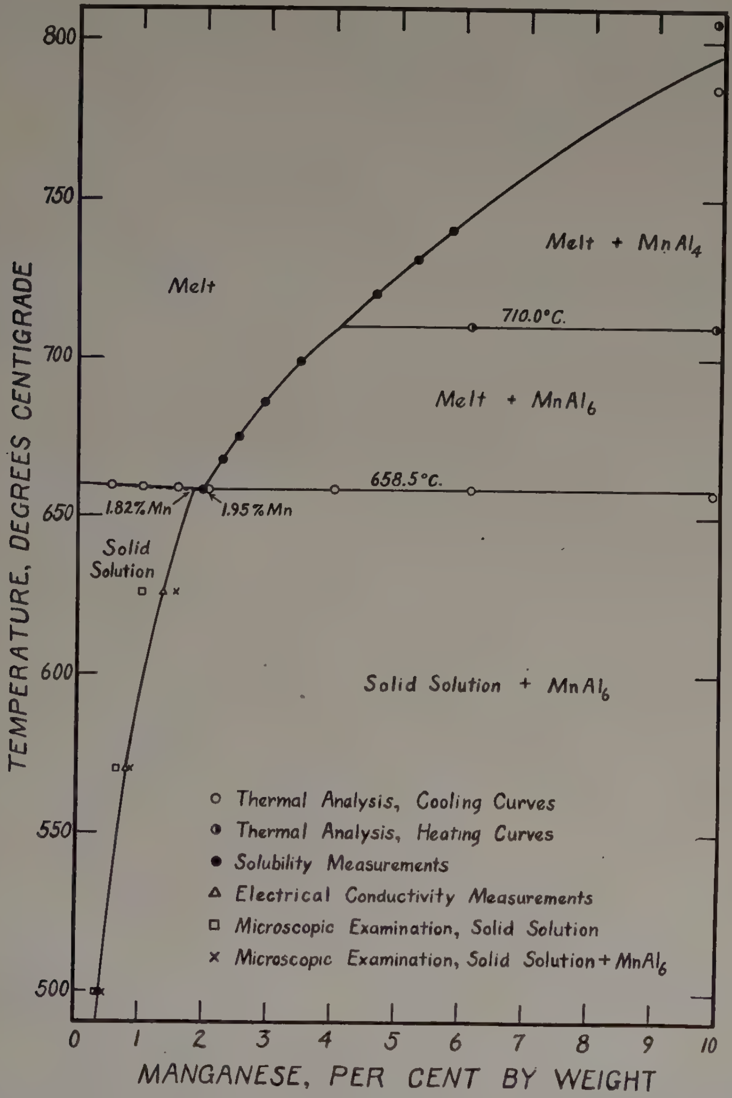

FIG. 22.—THE ALUMINUM END OF THE ALUMINUM-MANGANESE EQUILIBRIUM DIAGRAM.

By analysis of crystals separated from alloys quenched from above and below the peritectic reaction, by microscopic examination of heat-treated alloys having compositions corresponding to different possible compounds, and by X-ray analysis, the intermetallic compounds were found to have compositions that agreed within experimental error with the formulas $MnAl_6$ and $MnAl_4$. $MnAl_6$ is stable up to 710° C., where it decomposes to form $MnAl_4$ and liquid aluminum containing 4.06 per cent manganese in solution. Although there is evidence that $MnAl_4$ decomposes at a higher temperature, the corresponding peritectic horizontal has not been completely located.

ACKNOWLEDGMENT

The authors appreciate the assistance of Dr. K. R. Van Horn and Mr. H. V. Churchill, who supervised the X-ray and chemical analyses respectively. The authors are also indebted to Mr. C. S. Taylor for cooperation in connection with the electrical conductivity determinations.

Quantitative Estimation of the Impurities in Tin by Means of the Quartz Spectrograph*

By C. Stansfield Hitchen,† Cambridge, Mass.

(New York Meeting, February, 1933)

Abstract

The paper describes the application of the logarithmic wedge sector method of quantitative spectrography to the estimation of commonly occurring minor impurities in crude and refined tin. Both arc and spark methods of emission were employed and with the former a new device was used to overcome difficulties arising from the low melting point of the metal. The impurities investigated included antimony, arsenic, bismuth, copper, iron, lead, and zinc, their concentrations lying, in general, between 0.01 and 0.50 per cent. The results obtained show that the method may be usefully employed for the estimation of bismuth, copper, iron, lead, and zinc, in amounts ranging from 0.50 per cent to well below 0.01 per cent. Arsenic and antimony, however, could not be estimated in amounts less than 0.03 and 0.07 per cent respectively. Out of a total of 116 estimations by arc and spark emission, in 96 the errors were less than 5 per cent of the total quantity of the element present, whereas in the remaining twenty, the errors lay between 5 and 25 per cent. Spectro-analytical data for the several impurities studied are given in the form of tables, and curves correlating line-intensity with concentration have also been included.

DISCUSSION

(*R. G. Waltenberg presiding*)

D. M. Smith, London, England (written discussion).—I am interested in Dr Hitchen's account of his investigations on the application of spectrographic methods to the assay of tin and congratulate him on his valuable contribution to the literature on the subject of quantitative spectrum analysis. Some of the results obtained in the course of investigations carried out for the British Non-Ferrous Metals Research Assn., although obtained under somewhat different experimental conditions, may be of interest in connection with this paper.

Arc and spark spectra of standard samples of tin containing various known amounts of antimony, bismuth, cadmium, copper, lead, silver and arsenic have been investigated by means of the Hilger small quartz spectrograph, this instrument giving about one-third the dispersion of the medium size spectrograph used by Dr. Hitchen. For small quantities of impurities I prefer to use the simple internal standard method as applied to ordinary photographic records of spectra, the accuracy attainable being of the order of ±10 per cent on the estimated quantity. At the same time, I am of the opinion that of the photometric methods available for giving increased accuracy of estimation, the logarithmic sector method is certainly the most adaptable from the point of view of routine analytical work—especially for the higher percentages.

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* This paper is available at the office of the Institute as *Technical Publication No.* 494.

† Member of the Imperial College of Science and Technology, London. Commonwealth Fund Fellow, 1931–33.

It has been found that with metals of low melting point, such as tin and lead, the most satisfactory method of obtaining suitable graded series of standard alloys is to melt together in evacuated Pyrex glass tubes accurately weighed quantities of the constituent metals. For the tin alloys prepared in this way, a sample of tin was refined electrolytically under laboratory conditions, the metal obtained containing the following residual impurities: lead, 0.0026 per cent; antimony, less than 0.001; bismuth, 0.0004; copper, 0.0006; iron, 0.0003. With regard to the production of the spark, self-inductance was used to remove the air lines (which are more troublesome from the point of view of masking other lines when the small spectrograph is used), the amount used being sufficient to give equality of intensity between the arc line λ3330.6 and the spark line λ3352.3—by which means standardized and reproducible electrical conditions were obtained.[1]

For arc spectra, the arc between pure graphite electrodes, taking about 1.5 to 2 amp. was used. The sample was made the *negative* electrode, since it was found that under these conditions the spectra obtained closely resembled those of the arc between metallic electrodes, the cyanogen band at λ3883.4 (due to the graphite) being only very faintly present. With the short exposures used (15 to 20 sec.) the question of oxidation of the sample was not of great importance, but nevertheless Dr. Hitchen's device for maintaining the metal in a reduced condition is particularly ingenious and should be of wide applicability.

Under the conditions described above, it was found that smaller quantities of silver and bismuth (less than 0.001 per cent) could be detected by the spark method than by that of the arc; owing, no doubt, to the fact that the masking effect of the continuous background from λ3000 to λ4500 (approx.) is more pronounced in arc spectra than in spark spectra. For the rest, I have been able to detect as little as 0.015 per cent antimony, less than 0.001 per cent cadmium, 0.003 per cent lead, less than 0.0005 per cent copper but only 0.05 per cent arsenic by the methods I have used.

F. Twyman and A. Harvey, London, England (written discussion).—Recently we have been employing the same technique that Dr. Hitchen used, for the estimation of minor constituents of steels.[2] We have, however, employed a rather different method for plotting the results, which has the advantage that it often results in graphs that are straight lines over certain ranges of percentage. It has been shown by Twyman and Simeon[3] that the difference in the lengths of two lines is proportional to the logarithm of the ratio of the intensities of those lines, so it seemed to us logical to plot the length differences against *log %* rather than against the percentage itself. When this is done, a straight-line graph, $y = a + bx$, is often obtained. In many cases that we have examined this relationship is found to hold, over, at any rate, part of the ranges studied. As an example of this the figures given by the author in Table 2 have been plotted and give a straight-line relation of this type from 0.03 per cent up to 0.34 per cent. In view of the economy of labor that results when only two points are required in order to be able to draw one's reference curve, we recommend this method to future investigators in this field.

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[1] E. Schweitzer: *Ztsch. anorg. Chem.* (1927) **164**, 127–144.

[2] See *Jnl.* Iron and Steel Inst. (1932) **126**, 397.

[3] *Trans.* Opt. Soc. (1929–30) **31**, 172.

M. L. Fuller and G. W. Standen, Palmerton, Pa. (written discussion).—Any effort to remove errors of personal judgment in quantitative spectrographic analysis is highly commendable. Dr. Hitchen is to be congratulated for his contributions in this paper and in an earlier paper[4] on the logarithmic sector method of spectrophotometry.

The writers have investigated and applied various methods of spectrographic analysis, including the logarithmic sector method, and have made observations on the errors to be encountered which are pertinent to the present discussion. It has been our experience that it is difficult for two observers to agree upon the lengths of the lines in the wedge spectrum. Dr. Hitchen states that a line length cannot be measured to within less than 0.2 mm. This means that the line-length difference between the lines of a comparison pair is not significant for a difference of less than 0.4 mm. Inspection of the line-length difference-composition curves given in Dr. Hitchen's paper shows that this error in measuring line-length differences is of the same order of magnitude as the total error experienced in making analyses by this method.

It is because of this error inherent in the intensity measurement itself that the writers have continued to use a recording microphotometer (using a photoelectric cell) or the measurement of line intensity.[5] The error of measuring blackening is much less than the total errors involved in the analysis and thus no appreciable error is introduced by photometry.

G. Kuck, New York, N. Y. (written discussion).—Dr. Hitchen is to be thanked and praised for the completeness and the presentation of his work. Papers of a practical nature such as this are much needed. For any one spectrographic laboratory to thoroughly investigate all types of alloys that might come to them for analysis is a very large undertaking. The tendency, therefore, has been for each laboratory to specialize on one or two or three base metals. The services of a laboratory in the consulting field, however, are at the call of the industries served. This has its advantages, it is true, along the lines of broad endeavor and experience, but at the same time is a handicap in developing the technique on special items. As in the field of medicine, for example, the specialist and the general practitioner must each contribute of their experience and knowledge. Obviously, published work on the spectrographic analysis of alloys of all metals are important, but it is to be regretted that so far no papers as complete as Dr. Hitchen's have been published on nickel alloys, high-purity antimony, high-purity bismuth and copper alloys, using an internal standard.

The tables given in this paper will be useful not only to those using the internal standard, but also to those using the comparison method. The table on iron is especially useful. Recently, we have had occasion to use many of the lines quoted therein for the determination of iron in nickel wire.

Dr. Hitchen's observations on the difficulty experienced with copper are also met with in an arc spectrogram of nickel. However, there are a number of arc lines of copper, 2189.6, 2192.3, 2199.6, 2227.7 and 2230.1, which persist to 0.01 per cent in nickel, to 0.004 per cent in solution of zinc die casts, but only to 0.05 per cent in antimony-lead alloy. It is suggested that these same lines might be used in the analysis of tin.

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[4] F. Twyman and C. S. Hitchen: The Estimation of Metals in Solution by Means of Their Spark Spectra. *Proc.* Roy. Soc. (1931) **133A**, 72.

[5] For a description of the use of the photometer in this connection, see paper by C. C. Nitchie and G. W. Standen: *Ind. & Eng. Chem.*, Anal. Ed. (1932) **4**, 182.

In his discussion of the errors met with the author states that it may be due to "occasional inequalities in the light source" and "small-scale segregation." I believe he has omitted a third possible source of error that is caused by a difference in composition between the material under examination and the material used as standard; this difference being in the presence of different amounts of a third metal which is not being examined for. I refer to the phenomenon observed by Dr. Hitchen himself in another paper.[6] In that paper he stated that in the estimation of nickel and cobalt by means of the logarithmic wedge sector the curves were modified by the presence of iron or copper in solution. Nitchie[7] has also noticed that the presence of zinc and aluminum accentuates the intensities of lead lines in the arc spectrum of solutions containing both. From this, Mr. Nitchie concluded that it was necessary to use standards of nearly the same composition. In our practice, it is necessary that we know of these changes in intensities due to the presence of a third element. Can Dr. Hitchen advise whether he has found that the presence of any one metal in tin shifts the curves for the analysis of another metal?

E. H. S. van Someren, Birmingham, England (written discussion).—I agree with many of Dr. Hitchen's conclusions. In selecting his conditions for sparking he has eliminated as far as possible self-inductance from the discharge circuit. My experience is that such conditions result in reduced sensitiveness to lead, silver, copper, arsenic, antimony and bismuth. The difference of sensitiveness is illustrated by the fact that with 0.1 millihenry of self-inductance in the circuit I can easily detect 0.02 per cent of arsenic and 0.03 per cent of antimony in tin, while with no added self-inductance no lines of either element appear. This test was made using a spectrograph and plates similar to those used by Dr. Hitchen.

The method of obtaining a stable arc described by the author is interesting, but complicated. I have also tried a tin arc from 0.01 gram of tin in a carbon rod, but for uniformity and freedom from interference by iron lines I prefer to use the type of arc described (for lead) in my paper referred to by Dr. Hitchen.[8] With a current of 3 amp. in a tin arc adequate exposures can be made before the tin is sufficiently oxidized to disturb the spectrum, provided that no condensing lens is used.

In my experience the logarithmic sector is only reliable for comparing lines which are fairly similar in intensity and wave length. The comparison of line-pairs where one is 20 times as strong as the other (as in Fig. 9) or where one is blue and the other yellow (as for zinc, Fig. 8) may produce a smooth curve once, but is unlikely to give reproducible results in routine testing.

The problems of selecting the best conditions and the most suitable pairs of lines are of the utmost importance in quantitative spectrographic analysis. Some of the pairs of spark lines used by Dr. Hitchen are not among those quoted as homologous by Gerlach and Schweitzer and it would be interesting to know what degree of invariance is claimed for them.

H. E. Stauss, Newark, N. J.—We are chiefly concerned with qualitative analysis, but Dr. Hitchen has done work that might be carried over to it. He has compared the spectra of tin in both the arc and the spark. I wonder what his experience has been with regard to the relative sensitivities of the two methods in detecting the last traces of impurities, not for quantitative, but for qualitative, results. Which is more sensitive? With platinum we seem to find that the arc is the more sensitive. In the literature, at least in the past, preference seems to be given to the spark. Which is the correct view?

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[6] In the paper referred to in footnote 4.

[7] C. C. Nitchie: Quantitative Analysis with the Spectrograph. *Ind. & Eng. Chem.*, Anal. Ed. (1929).

[8] H. W. Brownsdon and E. H. S. van Someren: *Jnl.* Inst. Metals (1931) **46,** 97.

I should also like to ask Dr. Hitchen if he has had any experience with the interrupted arc that is described by Gerlach and Ruthardt; and if he has had, whether he believes it to have any advantages as compared with the continuous arc for detecting traces of impurities.

P. H. Brace, Pittsburgh, Pa.—I would like to ask a question as to the possibility of extending methods of this type to what might be regarded as gross analysis. For example, we may have from 3 to 5 per cent each of three or four different elements; as in alloy steels, for example. When melting scrap, particularly in electric-furnace practice, it would often be convenient to have a quick method of getting fairly accurate knowledge of the alloy content of a molten bath; for example, by drawing from the bath a small ladle of metal, casting it to form the electrode, using that immediately in an arc and thus, possibly by visual inspection of a sector of a wedge spectrum, obtaining reasonably accurate estimations, say within 10 per cent of the fairly large quantities of alloys present.

C. S. Hitchen (written discussion).—Dealing first with the points raised by Messrs. Fuller and Standen, it must be admitted that the logarithmic sector is not so accurate as the photoelectric photometer, nevertheless the actual gain in accuracy is not so great as might be at first supposed. By observing proper precautions and by taking the average of three sets of line-length measurements (see Table 2), it is possible to reduce considerably the photometric errors incurred with the sector, the final accuracy of estimation being slightly under 10 per cent of the total quantity of the substance present. This has been confirmed by a number of independent workers. The majority of the results in this paper show an accuracy greater than 10 per cent, but this is possibly the result of compensating errors.

As regards the photoelectric and other types of photometers, the consensus of opinion appears to be that only in exceptional circumstances is it possible to secure a greater accuracy than 5 per cent in ordinary industrial routine work. It is difficult to generalize in a field where errors are so largely determined by individual circumstances, but it would appear that the net gain in accuracy obtained by using a photometer in place of a sector is about 4 per cent. Against the superior accuracy of photometers must be set not only their high cost and delicate construction but the greater time required for carrying out an analysis.[9] The logarithmic sector, on the other hand, though less accurate photometrically, has much that commends it for industrial routine work. It is serviceable, speedy, relatively low in cost and can be used by an intelligent though unqualified assistant.

These remarks should not be interpreted as meaning that I wish to disparage the use of photoelectric and other types of photometers; on the contrary, I fully realize their potentialities and the fact that they are invaluable in certain phases of spectroanalytical practice. Many methods of quantitative analysis are now available and it becomes a matter of employing a method for the job to which it is best suited. I believe the sector possesses features that render it very well adapted for routine examinations, especially in smelting and other metallurgical operations.

Further in reply to Messrs. Fuller and Standen, I would point out that, while it is frequently found that the line-length measurements of two observers differ, the differences of length derived from their respective results are usually in close accord; *i. e.*, one observer consistently reads his line lengths "high" in relation to another.

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[9] In order that the full accuracy of the photometer method may be realized, it is essential that a calibration of the plate should be made, and this alone adds considerably to the time required for an analysis. When calibration of the plate is not included, the result would appear to be little, if any, better than those obtained with the sector.

The copper arc lines which Mr. Kuck mentions could doubtless be used for the analysis of copper in tin, but it would be necessary to increase the time of exposure somewhat, as these lines lie in a region where absorption effects commence to exert their influence. Errors arising from variation in the amount of a third element do not apply in the present case since the samples consisted only of tin. In alloys, however, samples and standards must be of comparable bulk composition. It is difficult to lay down any definite rules regarding the amounts by which major constituents may vary without affecting the accuracy of the analysis, as this depends not only upon the particular elements involved, but also upon the percentage range of the impurity being estimated. Each case would appear to require a separate investigation in this respect. I fear I cannot advise with certainty whether the presence of any one metal in tin affects the curves for the analysis of another metal as the work described in this paper was confined to more or less pure tin. Tin alloys, with which this effect would be more readily detected, were not investigated. I am able to state, however, that variation in the concentrations of the minor impurities had not the least effect on the accuracy with which each could be estimated.

In reply to Mr. Stauss, I would say that I believe the arc to be, in general, the more sensitive form of emission, especially for metals. For such elements as silicon, antimony, arsenic, and boron, the spark appears to possess advantages. So far I have not had an opportunity to investigate the interrupted arc of Gerlach and Ruthardt.

I believe the sector might be usefully applied to the type of problem outlined by Mr. Brace, provided that the total amount of minor metals does not exceed 5 per cent —in fact, Twyman and Harvey[10] have recently published a paper on a very closely related problem. Should the total amount of minor constituents range between 5 and 20 per cent, however, I think Barratt's "twin spark" method would prove more suitable, as this is as rapid as the logarithmic sector method and more accurate where higher percentages are involved.

An explanation of the differing experiences of Mr. van Someren and myself with regard to sensitivity and self-inductance is to be found, I think, in the times of exposure we employ, Mr. van Someren's being, apparently, of much shorter duration than mine.[11] *Intrinsically* the arc lines of arsenic and antimony are more sensitive than their spark lines, but such superior sensitivity can only be fully realized when the exposures are of a few seconds duration, owing to the ready volatility of these elements. The same would, I believe, apply in lesser degree when self-inductance is inserted in the circuit.

The use of carbon rods would almost certainly result in the appearance of some iron lines in the spectrogram. Acheson graphite, however, is very satisfactory in this respect and shows few lines due to impurity.

I agree that the best results are obtained when the lines of a line-pair are near together and of similar intensity, results tending to become less reproducable the greater the departure from similarity and proximity. We obtain fairly good results with a 1:10 ratio, while a 1:20 ratio is less satisfactory though not entirely impracticable. Naturally one does not use a poorer line-pair unless forced to do so by other cogent considerations. I am continually having to surrender otherwise good line-pairs owing to possible interference from lines of other substances likely to occur in the samples.

With regard to Mr. van Someren's final query, I would state that, once our best experimental conditions had been determined by a preliminary series of tests, a set of spectrograms was taken and a choice was made from the limited number of line-pairs available. The suitability of the selected line-pairs was confirmed by a second and third set of spectrograms taken at subsequent intervals.

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[10] F. Twyman and A. Harvey: Reference of footnote 2.

[11] Private communication.

The method of plotting advocated by Messrs. Twyman and Harvey has much to commend it since it is preferable to deal with straight lines than with curves. Nevertheless, while plotting *log %* against length differences results in a straight-line graph in many instances, in others a flattened curve is obtained, showing that the equation $y = a + bx$ does not entirely solve the relationship in such cases. In such circumstances two points would hardly yield an accurate reference curve and I suggest that at least four points should be available for its construction. Apart from this consideration, I believe the logarithmic plotting possesses advantages.

Quantitative Estimation of the Impurities in Tin by Means of the Quartz Spectrograph

By C. Stansfield Hitchen,* Cambridge, Mass.

(New York Meeting, February, 1933)

The introduction of the logarithmic sector method of quantitative spectrography by Scheibe and Neuhäusser in 1928, and the subsequent modification and improvement of the method by Twyman and Simeon, would seem to have marked yet a further advance in quantitative spectrum analysis and its industrial application, inasmuch as it offers a simple means of eliminating some of the uncertainties inherent in the older methods based upon mere visual comparison of line intensities. In their recent admirable review of the position and capabilities of industrial spectroscopy, Brownsdon and van Someren[1] say:

> Ways and means of facilitating the comparison of line-intensities so as to give them numerical values are helpful, and of these a logarithmic sector rotating in front of the slit appears to be one of the most promising; . . .

The success recently experienced by the author in using this method for the examination of steels and solutions of metallic salts prompted him to investigate its possible use in estimating the impurities commonly present in crude and refined tin. The results of this investigation are submitted in the present paper.

Details of a number of spectrographic analyses of tin for various impurities have already been published. Thus, Schweitzer[2] describes the spectrographic examination of tin for lead, bismuth and cadmium, and was able to distinguish between such atomic percentages as 0.01, 0.05, 0.10, 0.30, 0.60, 1.20, 3.00 and 10.00. Negresco[3] investigated the bismuth content of tin over a range of from 0.0005 to 35 per cent. Meggers, Kiess and Stimson[4] compare spectrographic and chemical analyses of tin metal for copper, lead, iron, zinc, silver, nickel and bismuth. They stress also the value of spectrum analysis in the examination of tin used for boiler plugs, where the requirements that only minute quantities of impurities shall be present render the chemical analysis both tedious and difficult.

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* Member of the Imperial College of Science and Technology, London. Commonwealth Fund Fellow, 1931–33.

[1] H. W. Brownsdon and E. H. S. van Someren: *Jnl.* Inst. Metals (1931) **46,** 97.

[2] E. Schweitzer: *Zsch. f. anorg. u. allg. Chem.* (1927) **164,** 127.

[3] T. Negresco: Recherches Expérimentales d'Analyse Spectrale Quantitative sur les Alliages Métalliques. Les Presses Universitaires de France, 1927.

[4] W. F. Meggers, C. C. Kiess, and F. J. Stimson: U. S. Bur. Stds. *Sci. Paper* 444 (1922) 325.

Further data concerning the spectrographic analysis of tin for bismuth, cadmium and lead is given by Gerlach and Schweitzer.[5] Various methods were adopted by the authors mentioned for measuring the intensities of lines due to the particular impurities investigated. Thus Meggers, Kiess and Stimson matched the intensities with the brightness of an electrically heated tungsten wire, while Negresco employed a microphotometer consisting of a photoelectric cell and galvanometer. Schweitzer employed the "internal standard" method, in which the intensity of a line due to the impurity was compared with that of a line due to the main constituent. As far as is known, the only previous application of the logarithmic sector method to estimating impurities in tin was the original work carried out by Scheibe and Neuhäusser,[6] in which they employed their newly devised logarithmic sector to determine lead in tin over a range of from 0.10 to 3.00 per cent.[7]

While a considerable amount of valuable information is therefore available, a greater part of it is somewhat restricted in nature and no work appears to have been carried out with a view to providing tin smelters, and others commercially interested in tin, with such data as would enable them to examine their product spectrographically for all the commonly occurring impurities; namely, bismuth, copper, iron, lead, zinc, arsenic and antimony. The present work was undertaken therefore, with the object of establishing a procedure whereby all these impurities could be quantitatively determined in the same spectrogram over such ranges of concentration as are commonly met with in practice.

Space does not permit here of a discussion of the principles involved in the logarithmic sector method nor of the general technique employed; these have, however, been adequately described in papers by Twyman and Simeon,[8] Twyman and Fitch,[9] and Twyman and Hitchen.[10]

APPARATUS AND TECHNIQUE

Owing to the comparative simplicity of the tin spectrum, a quartz spectrograph of medium dispersion by Hilger (E.316) was chosen. Other apparatus employed consisted of a suitable quartz condensing lens, a Gramont stand for holding electrodes, a logarithmic sector mounted on a clockwork motor, and electrical apparatus for the production of arc and spark discharge. The arrangement of this apparatus and the general technique adopted were precisely as described by Twyman and Hitchen.

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[5] W. Gerlach and E. Schweitzer: Foundations and Methods of Chemical Analysis by the Emission Spectrum. Authorized translation of Die Chemische Emissionsspektralanalyse. Hilger, 1931.

[6] G. Scheibe and A. Neuhäusser: *Ztsch. f. angew. Chem.* (1928) **41,** 1218.

[7] The spectrographic estimation of lead in tin alloys has been studied more recently by G. Scheibe, C. F. Linström, and O. Schnettler: *Ztsch. angew. Chem.* (1931) **44,** 145.

[8] F. Twyman and F. Simeon: *Trans.* Opt. Soc. (1929–30) **31,** 169.

[9] F. Twyman and A. A. Fitch: *Jnl.* Iron and Steel Inst. (1930) **122,** 289.

[10] F. Twyman and C. S. Hitchen: *Proc.* Roy. Soc. (1931) **133A,** 72.

Spark Method.—Excitation was provided by a ¼-kw. transformer and autotransformer similar to the unit described and illustrated in the paper by Twyman and Hitchen (p. 74 and Fig. 2). Preliminary experiments showed that while the inclusion of self-induction in the spark circuit minimized the effect of air lines, it definitely detracted from the spectroscopic sensitivity of some of the elements, notably arsenic and antimony, therefore in later experiments it was omitted.

A condensed spark of 15,000 volts on open circuit, without self-induction, was maintained throughout the tests, the electrodes being 3 mm. apart. The latter were chisel-shaped, the blunted edges being set parallel to the axis of the collimator. With a slit width of 0.04 mm. and a 1 by 1⅜-in. (oval) stop, the time of exposure required was 90 sec. A planoconvex condensing lens working at distances of 70 cm. from the collimator lens and 19 cm. from the light source was employed.

Arc Method.—The maintenance of an arc discharge between small bars of tin proved a somewhat difficult matter, owing to the low melting point of the metal, and it was necessary to devise some other method. After considerable experimentation, the following procedure was adopted.

The end of a graphite rod, ⅜ in. in diameter, was scooped out with the aid of a drill and ordinary carpenter's countersink, into a cuplike cavity capable of holding between one and two grams of the tin sample. This was then fixed in the Gramont stand as the lower and positive electrode, while the upper negative electrode consisted of a similar graphite rod, ¼ in. in diameter, tapered to a point by means of a pencil-sharpener, as shown in Fig. 1. After the arc had been running for several minutes under these conditions it was found that a considerable quantity of stannic oxide had collected around the electrodes and upon the surface of the metal. Owing to the possible effects that this might have upon the quantitative results, it was considered necessary to find some means of keeping the metal in a reduced condition and this was finally accomplished by the use of a small luminous coal-gas flame directed on to the surface of the molten tin. At first a little practice was required in regulating the jet to make it cover the surface of the tin and yet be not strong enough to sever the arc. With an arc current of 3 amp. and a convex condensing

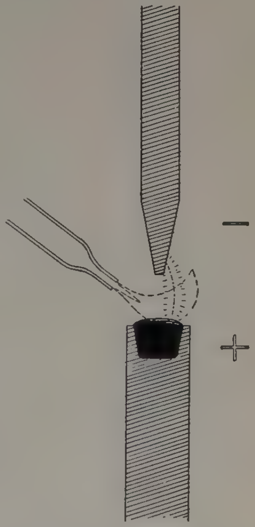

FIG. 1.—METHOD OF MAINTAINING ARC DISCHARGE WITH A SMALL AMOUNT OF TIN.
Graphite rods with tin in cup of lower rod.

lens placed 26 cm. from the slit and 26 cm. from the light source, the exposure required amounted to 30 sec. A slit width of 0.02 mm. and a ⅝ by ⅞-in. (oval) stop were employed.

In taking spectrograms either with the arc or spark, it is first necessary to bring the electrodes centrally within the lens aperture of the spectrograph; it is also important that the speed of the logarithmic sector should be maintained at approximately 300 revolutions per minute.

Photography.—Rapid process panchromatic plates,[11] used in conjunction with a restrained hydroquinone developer, have been found most generally satisfactory for wedge-sector spectrophotometry, and were employed throughout the present investigation. For full details of the photographic technique employed, the reader is referred to papers by Twyman and Hitchen[12] (p. 91) and Twyman and Harvey.[13] It should be stressed here that the success of the wedge-sector method largely depends upon a rigorously standardized photographic procedure with time-temperature control of development.

Measurement of Line Lengths.—Measurement of the lengths of the lines in the wedge spectrum is effected by the use of a small eyepiece, provided with a 20-mm. scale divided into tenths of a millimeter and having a magnification of 12. The plates are viewed either by light reflected through the plate from a plain white surface or by light transmitted through a screen of opal glass, the essential point in both cases being that the illumination shall be of a bright and even character.

Beginners frequently experience some difficulty in locating the termination of the lines but after a little practice fairly concordant results are obtained. It is difficult to measure a line length to within less than 0.2 mm. and higher magnifications than 12 tend to confuse the observer rather than to help him.

ANALYTICAL INTERPRETATION OF WEDGE SPECTROGRAMS

In the logarithmic sector method, as in most other methods of quantitative spectrography, the general procedure consists of first correlating the increase in intensity (or some function of the intensity) of a suitable line (or lines) of the element to be determined, with increasing percentage, this being accomplished by means of a series of either carefully analyzed or artificially prepared standard samples covering the desired range. The relationship between line intensity (or some function of the intensity) and percentage, thus determined, is usually shown by means of a table or graph, which can be afterwards referred to for the analysis of unknown samples.

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[11] Ilford Rapid Process Panchromatic plates, 10 by 4 in., thin glass. Speed: Watkins 110, Wynne 67. Wratten Process Panchromatic plates are essentially similar to the Ilford plates and may be substituted for them. They have a somewhat higher speed and, particularly, a higher green sensitivity, but their contrast characteristics are about the same with equal development.

[12] Reference of footnote 9.

[13] F. Twyman and A. Harvey: *Trans.* Opt. Soc. (1931–32) **33,** 1.

The effect of the logarithmic sector is to produce wedge spectra (Fig. 10) in which the length of a line is a function of its intensity, and hence of the concentration of the element to which its presence is due. The line length cannot be directly used for analytical purposes, however, because other factors, such as electrical and photographic conditions, exert a considerable influence upon it. Since some of these factors cannot be standardized beyond a certain and insufficient limit, the direct length still remains too inaccurate a criterion for analytical purposes.

Under these circumstances the "internal standard" method of Gerlach[14] is adopted, whereby the intensity of a chosen line of the element to be determined is measured in relationship to a neighboring line given either by the major constituent (in this case tin) or an element occurring in the samples in a known and constant amount. Then, provided that fluctuating electrical conditions cause no serious change in the *relative intensities* of the two selected lines, experimental conditions will affect both lines alike, and the line of the "internal standard," whether of the major constituent or an added element, may be used for gaging the true intensity of the line of the element it is desired to estimate. Two such lines, one due to the internal standard and the other to the element, will be referred to hereafter as a "line-pair."

In their original paper on the wedge sector method, Scheibe and Neuhäusser took the following ratio:

$$\frac{\text{Length of line of element to be estimated}}{\text{Length of line of internal standard}}$$

They plotted this against percentage. Twyman and Simeon,[15] however, have shown that such a procedure is not justified by theory and that the *difference of length* between the two lines should be plotted against the percentage. In the present paper this latter course has been adopted.

It is impossible to discuss here the selection of line-pairs, the determination and use of homologous and fixation pairs of lines, and the possibility of fluctuating electrical conditions affecting the relative intensities of lines constituting a line-pair. These and other matters have been fully discussed by Gerlach and Schweitzer[16] and by Twyman and Hitchen,[17] and the reader is referred to these sources for further information on this aspect of the subject.

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[14] W. Gerlach: *Ztsch. f. anorg. Chem.* (1925) **142,** 385.

[15] Reference of footnote 7.

[16] Reference of footnote 5.

[17] Reference of footnote 9.

ANALYSES OF SAMPLES

The samples, which were prepared and analyzed by Mr. Carrott, of the Thames Metal Co., London, England, were in the form of bars 5 in. long and ¼ in. in diameter. The portions of the bar used for spectrographic analysis were taken midway between the center and ends. The analyses of the bars (numbered 1 to 60) are given in Table 1. The amounts of the various elements occurring as impurity in tin metal should normally fall within the ranges of percentages given in that table.

TABLE 1.—*Analyses of Samples*

Arsenic		Antimony		Bismuth		Copper		Iron		Lead		Zinc	
Bar No.	Content, Per Cent	Bar No.	Content, Per Cent	Bar No.	Content, Per Cent	Bar No.	Content, Per Cent	Bar No.	Content, Per Cent	Bar No.	Content, Per Cent	Bar No.	Content, Per Cent
28	0.03	10	0.032	52	0.01	36	0.01	44	0.01	60	0.01	23	0.02
27	0.05	7	0.05	5	0.03	4	0.026	43	0.02	59	0.02	22	0.03
7	0.059	9	0.073	51	0.04	35	0.03	42	0.03	7	0.027	21	0.04
26	0.07	4	0.08	50	0.05	7	0.04	41	0.04	58	0.04	20	0.05
25	0.08	8	0.10	49	0.06	34	0.05	5	0.05	57	0.05	19	0.06
5	0.09	6	0.52	48	0.07	33	0.06	40	0.06	56	0.06	18	0.07
1	0.13			47	0.08	32	0.07	39	0.07	55	0.08	17	0.12
14	0.53			46	0.09	31	0.08	38	0.08	54	0.09	16	0.22
				45	0.10	30	0.09	37	0.10	53	0.10	15	0.44
				12	0.23	1	0.10	1	0.22	5	0.18		
						5	0.29	11	0.34	1	0.35		
						29	0.40			12	0.60		
						13	0.61			3	0.88		

RESULTS

For the sake of conciseness, the results of the present investigation are given in the form of tables and graphs. The former indicate which of the principal lines of each element are best suited for use in the analysis of tin by both arc and spark methods. Information regarding their persistency, intensity, and the possibility of their being masked, etc., will be found in the "Remarks" column of each table; it should be pointed out, however, that such information, especially that relating to intensity, is strictly valid only for spectrograms taken under experimental conditions identical with those referred to and described under the heading "Apparatus and Technique" earlier in this paper. The graphs given in Figs. 2 to 9 show the difference in length of selected line-pairs plotted as ordinates against percentages as abcissas. In the construction of these graphs it has been necessary to adopt the following convention: When the line of the element to be estimated is *longer* than the line of the internal standard, the difference is designated as *positive*.

Owing to reasons of space, it will be impossible to reproduce here the complete set of line-length measurements from which the curves were constructed, but the exscript given in Table 2 will serve as an example.

TABLE 2.—*Example of Line-length Measurements*[a]

IRON in Tin; line-pair used $= \dfrac{\text{Fe}\begin{cases}3021.077\\3020.645\end{cases}}{\text{Sn}\quad 3141.81}$ Arc ("gas-flame" method).

Fe, Per Cent	Fe $\begin{cases}3021.077\\3020.645\end{cases}$ Length, Mm.			Sn 3141.81 Length, Mm.			Difference in Length, Mm.			Average Difference
	a	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*	
0.01	7.0	6.9	7.1	13.0	13.0	13.0	−6.0	−6.1	−5.9	−6.0
0.02	7.4	7.3	7.6	13.1	13.0	13.0	−5.7	−5.7	−5.4	−5.6
0.03	7.8	8.0	8.1	13.0	13.0	13.2	−5.2	−5.0	−5.1	−5.1
0.04	8.2	8.4	8.4	13.1	13.0	12.9	−4.9	−4.6	−4.5	−4.7
0.05	8.7	8.9	9.1	13.6	13.5	13.5	−4.9	−4.6	−4.4	−4.6
0.06	9.1	9.3	9.3	13.3	13.4	13.3	−4.2	−4.1	−4.0	−4.1
0.07	9.7	9.4	9.8	13.0	13.0	13.1	−3.3	−3.6	−3.3	−3.4
0.08	9.7	9.8	9.9	13.0	13.2	13.1	−3.3	−3.4	−3.2	−3.3
0.10	9.3	9.7	9.8	12.6	12.7	12.5	−3.3	−3.0	−2.7	−3.0
0.22	11.4	11.2	11.2	13.4	13.2	13.0	−2.0	−2.0	−1.8	−1.9
0.34	11.6	11.7	11.8	12.4	12.7	12.7	−0.8	−1.0	−0.9	−0.9

[a] Three sets of readings, *a*, *b*, *c*, were taken at intervals by the same observer.

TABLE 3.—*Principal Lines of Bismuth Best Suited for Use in Analysis of Tin*

SPARK, SENSITIVE LINES

Wave Length, IA	Remarks
3067.73	Most sensitive, persisting to 0.01 per cent Bi. May be measured with the tin line 3141.81.
2989.04	Does not occur below 0.10 per cent Bi.
2938.31	Masked by a band of the tin spectrum.
2897.98	Does not occur below 0.10 per cent Bi.
2780.52	Masked by the tin line 2779.81.

ARC, SENSITIVE LINES

4722.7 4722.5 4722.2	Persist down to 0.01 per cent Bi, but unsuitable for measurement in presence of Zn owing to the zinc line 4722.163.
3067.73	Most sensitive continuing to appear down to 0.001 per cent Bi. Unfortunately this line is masked by iron (3067.253).
2897.98	Persists to well below 0.01 per cent Bi, but masked by iron when it exceeds 0.20 per cent. May be measured against Sn, 2787.9.

The following homologous pairs are given by Gerlach and Schweitzer[18] for the analysis of Bi in Sn in the spark spectrum (wave lengths given to the nearest whole number):

Bi............	3068	2697	2938	2628	2938	3068	3019	3068
Sn............	3009	2765	3142	2637	2765	3142	3219	3224

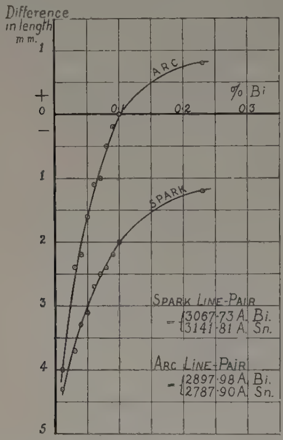

FIG. 2.—INTENSITY-COMPOSITION CURVES FOR BISMUTH (ARC AND SPARK EMISSION).

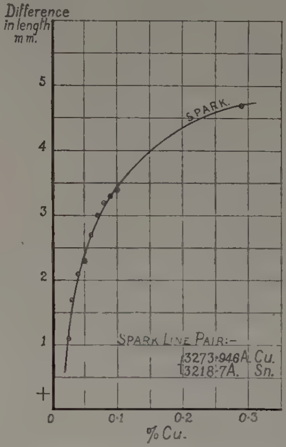

FIG. 3.—INTENSITY-COMPOSITION CURVE FOR COPPER (SPARK EMISSION).

TABLE 4.—*Principal Lines of Copper Best Suited for Use in Analysis of Tin*

SPARK, SENSITIVE LINES

Wave Length, IA	Remarks
4378.17	Appears in the spectrum only when copper exceeds 0.10 per cent.
3273.964 3247.548	This well-known copper doublet is extraordinarily sensitive, persisting to 0.001 per cent Cu. The tin line 3218.7 is suitable as a standard for measurement.
2529.43	Seen faintly in the spectrum of tin containing 0.01 per cent Cu.
2369.91	Persists to 0.01 per cent Cu but liable to be masked by As 2369.7 and Fe 2369.59.

ARC, SENSITIVE LINES

5105.551^{a}	Seen faintly with 0.01 per cent Cu but owing to its occurrence in the visible region this line is unsuitable for measurement when the "gas-flame" method (p. 5) is employed.
4063.293 4062.694 ^{a}	Persist down to 0.01 per cent Cu but measurement is difficult and unsatisfactory in presence of Pb (Pb, 4057.8).
3273.967 3247.550 ^{a}	Extraordinarily sensitive. Too strong for length measurements until Cu falls to 0.05 per cent. Excellent for qualitative work.
2961.177^{a}	Persists down to 0.03 per cent Cu. May be used for measurement with Sn 2787.9 as a standard.
2824.378^{a}	Seen faintly in the spectrum of tin containing 0.01 per cent Cu. Unsuitable for measurement.
2766.388^{a}	Seen faintly with 0.30 per cent Cu.
2618.381^{a}	Seen faintly with 0.06 per cent Cu.

[a] Hasbach's values [*Ztsch. wiss. Phot.* (1914) **13,** 399–430].

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[18] Reference of footnote 5.

The curves of Fig. 2 were constructed from measurements of the spark line-pair $\frac{\text{Bi } 3067.73}{\text{Sn } 3141.81}$ and of the arc line-pair $\frac{\text{Bi } 2897.98}{\text{Sn } 2787.90}$.

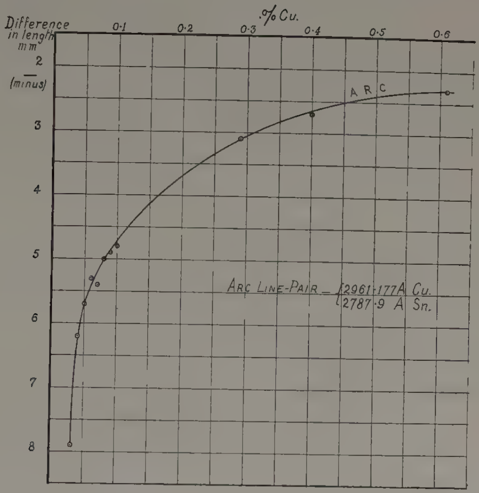

FIG. 4.—INTENSITY-COMPOSITION CURVE FOR COPPER (ARC EMISSION).

The arc lines of copper are not so well adapted to quantitative estimation as are those of the other elements, owing to the unbalanced character of their intensities and persistencies. Thus, while the well known doublet, 3274-3247, is extraordinarily sensitive and usually appears too strong for length measurements, the remaining copper lines possess comparatively poor sensitivity. For purposes of quantitative spectrographic estimation, the spark lines of this element are far superior.

Curves are given for the spark line-pair $\frac{\text{Cu } 3273.964}{\text{Sn } 3218.7}$ and the arc line-pair $\frac{\text{Cu } 2961.177}{\text{Sn } 2787.9}$ (Figs. 3 and 4).

In Table 5 are given the sensitive spark lines for iron as confirmed during the present investigation. Owing to their larger number, the scheme of tabulation adopted differs slightly from that employed in Tables 3 and 4. Where a sensitive iron line is liable to be masked by the line of another element occurring in tin samples, the symbol of that element and the wave length of the interfering line are given in brackets after the iron line.

Fig. 5 shows a curve obtained by plotting difference of length of the spark line-pair $\frac{\text{Fe } 2382.04}{\text{Sn } 2380.75}$ against percentage of Fe.

The arc spectrum of tin containing 0.30 per cent of iron exhibits a considerable number of lines due to the latter element which tend to arrange themselves in groups between 5700A in the visible and 2450A in

TABLE 5.—*Principal Lines of Iron Best Suited for Use in Analysis of Tin*

SPARK, SENSITIVE LINES

	WAVE LENGTH, IA	
	3820.430	Persists to 0.10 per cent Fe.
	2755.74 (Zn 2756.4)	Possess good intensity, even at 0.01 per cent Fe and should persist to well below this percentage.
Grow faint at 0.01 per cent Fe, but still visible	2753.29	
	2749.324 (Cd 2748.67)	
	2748.987	
	2746.486	
	2743.199	
	2739.551	
	2611.88 (Sb 2612.31)	Seen in the spectrum of tin containing 0.01 per cent Fe.
	2607.098	
	2599.40 (Cu 2600.4)	
	2598.377 (Sb 2598.077)	
	2585.884	
These lines occur very faintly in the spectrum of tin containing 0.01 per cent Fe.	2413.312	
	2411.07	
	2410.53	
	2406.66	
	2404.886 (Cu 2403.4)	Medium intensity at 0.01 per cent Fe.
	2399.24 (Cu 2400.10)	
	2395.63	Most sensitive lines possessing good intensity at 0.01 per cent Fe. Should persist to 0.001 per cent.
	2388.63	
	2382.04	

ARC, SENSITIVE LINES

	4957.606	This characteristic group, seen in the visible spectrum of the iron arc, occurs only when iron exceeds 0.10 per cent.
	4920.521	
	4890.770	
	4872.149	
Faint at 0.02 per cent Fe.	4415.128 (Cu 4415.6)	
	4404.754	
	4383.549	Well defined at 0.02 per cent Fe.
	4325.768	
	4307.909 (Bi 4308.2)	
	4271.765	
	3647.845	Suitable for measurement against Sn 3655.92 A but disappear when Fe falls below 0.02 per cent.
	3631.465	
	3617.789	
	3608.861 (Cd 3610.510)	
	3440.612	Persists to 0.01 per cent Fe.
	3021.077	Suitable for measurement with Sn 3141.8 A. Well defined at 0.01 per cent Fe. (The Zn line at 3018.38 does not usually interfere.)
	3020.645	
Occur as faint lines in the spectrum of tin containing 0.01 per cent Fe.	2994.436	
	2983.571	
	2973.236	
	2966.901	
	2957.370	Disappear when Fe falls to 0.02 per cent.
	2953.943	
	2947.879	
	2936.904 (Bi 2938.31)	
	2750.145	Disappear when Fe falls below 0.03 per cent.
	2742.408	
	2736.971	
Disappear at 0.04 per cent Fe.	2733.579	
	2723.582	
	2720.909	This doublet seen faintly with 0.01 per cent Fe.
	2719.036 (Sb 2718.91)	
	2613.835	Well defined at 0.01 per cent Fe but masked by Pb 2613.68.
Disappears at 0.04 per cent Fe.	2599.577	
	2598.380 (Sb 2598.077)	Seen faintly with 0.01 per cent Fe.
	2527.44	Disappears at 0.06 per cent Fe.
	2522.855	Disappears at 0.03 per cent Fe.
	2518.107	Disappear at 0.01 per cent Fe.
	2510.839	
	2501.136	
	2488.148	Disappears at 0.03 per cent Fe.
	2483.277	Masked by Sn 2483.4.

the ultra violet. When the percentage of iron is decreased, many of these lines disappear but some persist to 0.01 per cent Fe, and may interfere with certain lines due to other elementary impurities which it is desired to estimate. Before searching the spectrogram for these latter lines therefore, it is advisable to observe the number and intensity of the iron lines. A little practice should enable the observer to assess the amount of iron present with fair precision by a mere visual inspection of the plate. A curve is given (Fig. 6) for the arc line-pair $\frac{\text{Fe}\begin{Bmatrix}3021.077\\3020.645\end{Bmatrix}}{\text{Sn } 3141.81}$.

TABLE 6.—*Principal Lines of Lead Best Suited for Use in Analysis of Tin*

SPARK, SENSITIVE LINES

Wave Length, IA	Remarks
4057.830	Given by de Gramont as the most sensitive line but masked by an air line at 4057.8.
3683.472	Persists to 0.01 per cent Pb but is difficult to read when Pb is below 0.03 per cent. The tin lines suitable as standards are 3655.92 and 3218.7.
3639.584	Persists to 0.04 per cent Pb but an air line at 3639.6 renders readings difficult. May also be masked by 3637.83 given by relatively high contents of Sb.
2873.32	Persists to 0.06 per cent Pb.
2833.069	Persists to 0.01 per cent Pb. Suitable for measurement.
2802.007	Does not appear when Pb is below 0.02 per cent.
2663.17	Does not appear when Pb is below 0.02 per cent.
2614.203 2613.68	Disappears at 0.05 per cent Pb. Unsuitable for measurement, being masked by a band and Fe 2613.84.
2577.280	Only seen when lead exceeds 0.50 per cent.
2203.5	Does not appear when Pb is below 0.10 per cent.

ARC, SENSITIVE LINES

Wave Length, IA	Remarks
4057.830	Very strong, persisting down to 0.001 per cent Pb. Liable to masking by 4057.87 due to Zn.
3683.47	Very strong. Suitable for measurement against Sn 3655.92.
3671.50	Persists down to 0.01 per cent Pb.
3639.584	Similar to 3683.47 above. Suitable for measurement.
2873.32	Well defined at 0.01 per cent Pb. Liable to masking by Fe 2874.17.
2833.069	Very strong. Should persist to 0.001 per cent Pb.
2823.199	Well defined at 0.01 per cent Pb. Masked by Fe 2823.28.
2802.007	Very strong. Unsuitable for measurement in presence of relatively large amounts of Zn (Zn 2802.00).
2663.17	Well defined at 0.01 per cent Pb.
2614.203 2613.68	Well defined at 0.01 per cent Pb. Masked by Fe 2613.84.
2577.84	Disappears at about 0.05 per cent Pb.
2476.39	Seen faintly in the spectrum of tin containing 0.02 per cent Pb.

According to Gerlach and Schweitzer the following are homologous pairs of lines in the spectra of tin containing lead as an impurity (wave lengths given to nearest whole numbers):

Pb........	2833*	2663*	2802	4058	2614*	2823*	2873*	2802	4058	2614
Sn.........	2851	2661	2851	3801	2594	2765	2765	2765	3656	2637

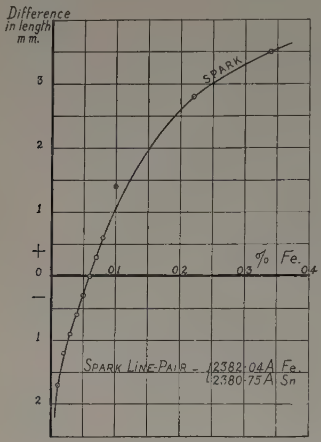

FIG. 5.—INTENSITY-COMPOSITION CURVE FOR IRON (SPARK EMISSION).

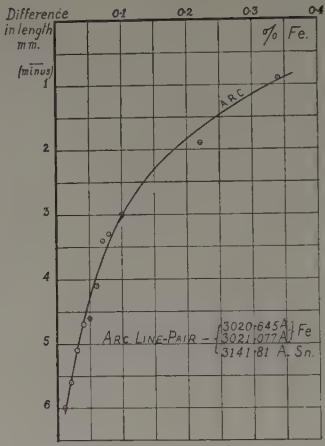

FIG. 6.—INTENSITY-COMPOSITION CURVE FOR IRON (ARC EMISSION).

The line-pairs marked with an asterisk were used by Scheibe and Neuhäusser in their original experiments with the logarithmic sector.

TABLE 7.—*Principal Lines of Zinc Best Suited for Use in Analysis of Tin*

SPARK, SENSITIVE LINES

Wave Length, IA	Remarks
4810.534	Does not occur below 0.10 per cent Zn.
4722.163	Does not occur below 0.20 per cent Zn. Masked by Bi.
3345.9 3345.51 3344.91	Suitable for measurement against Sn 3218.7. Disappears at about 0.02 per cent Zn.
3302.91 3302.56	Suitable for measurement against Sn 3218.7. Persists to 0.01 per cent Zn.
2138.5	Seen faintly in the spectrum containing 0.4 per cent and 0.2 per cent Zn.

ARC, SENSITIVE LINES

Wave Length, IA	Remarks
4810.534	Persists to below 0.01 per cent Zn. Suitable for measurement against Sn 5631.92.
4722.163	Persists to below 0.01 per cent Zn. Masked by Bi triplet.
4680.140	Persists to below 0.01 per cent Zn. Masked by Fe, 4678.855 above 0.10 per cent.
3345.51 3344.91	Persists to below 0.01 per cent Zn. Suitable for measurement with Sn 3218.7 as standard.
3302.91 3302.56	Persists to below 0.01 per cent Zn. There is possibility of interference by Na lines 3302.94 and 3302.34.
3282.32	Unsuitable for measurement being masked by an unknown line (due either to AgTi, or Cu).

The curves given in Fig. 7 are for the spark line-pair $\frac{\text{Pb } 3683.47}{\text{Sn } 3218.7}$ and the arc line-pair $\frac{\text{Pb } 3639.58}{\text{Sn } 3655.92}$. With regard to the arc spectrum, it was found that this line-pair was unsuitable for amounts of lead above 0.35 per cent, owing to the strength of the lead line. For its estimation above this percentage, the line-pair $\frac{\text{Pb } 2873.32}{\text{Sn } 3218.7}$ may be employed.

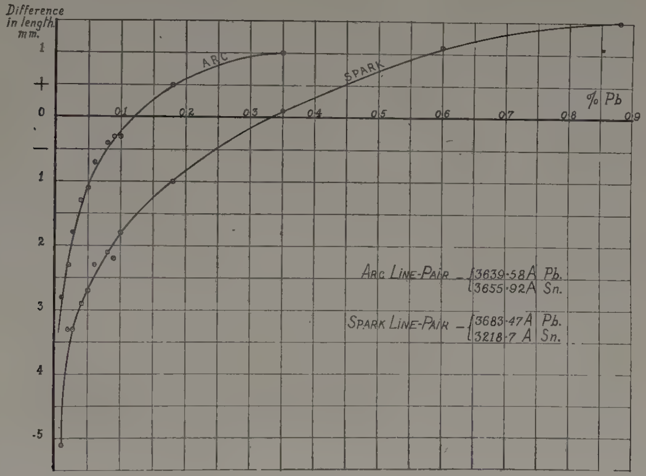

FIG. 7.—INTENSITY-COMPOSITION CURVES FOR LEAD (SPARK AND ARC EMISSION).

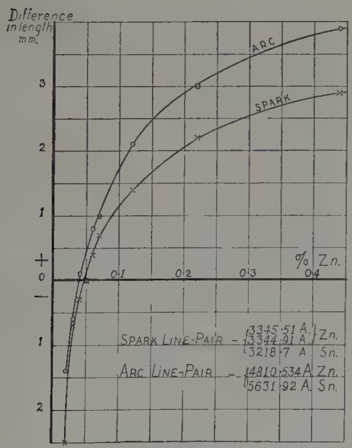

FIG. 8.—INTENSITY-COMPOSITION CURVES FOR ZINC (SPARK AND ARC EMISSION).

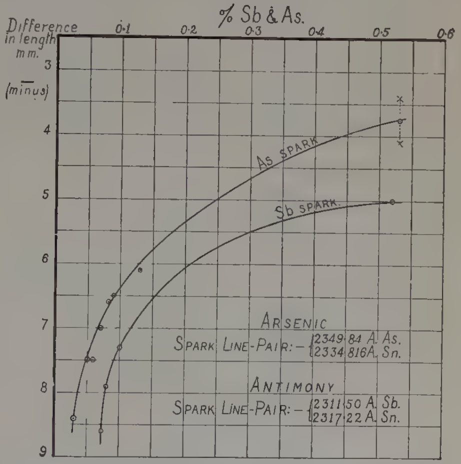

FIG. 9.—INTENSITY-COMPOSITION CURVES FOR ARSENIC AND ANTIMONY (SPARK EMISSION).

The three arc lines for zinc, 4810.534, 4722.163 and 4680.140, are very striking and characteristic, and can be discerned at a glance in the spectrum of tin containing only 0.01 per cent Zn. Curves are given in Fig. 8 for the spark line-pair $\frac{\text{Zn}\left\{\begin{matrix}3345.51\\3344.91\end{matrix}\right.}{\text{Sn } 3218.7}$ and the arc line-pair $\frac{\text{Zn } 4810.534}{\text{Sn } 5631.92}$.

TABLE 8.—*Principal Lines of Antimony Best Suited for Use in Analysis of Tin*

SPARK, SENSITIVE LINES

Wave Length, IA	Remarks
3267.48	Does not appear with 0.52 per cent Sb.
3232.52	Appears with 0.52 per cent but not with 0.20 per cent Sb.
2598.077	Most sensitive line but masked by Fe 2598.380 which appears with low percentages of iron.
2528.53	Coincides with Si 2528.516 and As 2528.4, the latter appearing with 0.10 per cent As.
2311.50	Useful for estimating Sb in tin from 0.07 per cent to 3 to 4 per cent. The tin line 2317.22 may be used as a standard.

ARC, SENSITIVE LINES

Wave Length, IA	Remarks
2877.92	If iron does not exceed 0.10 per cent, this line may be measured and persists to 0.07 per cent Sb.
2769.94	Masked by Zn 2770.85, which appears with very low percentages of that element.
2598.077	Sensitive but masked by Fe 2598.380.
2528.53	Sensitive but masked by Fe 2529.139.
2311.50	May be used when iron does not exceed 0.10 per cent and is sensitive to 0.07 per cent Sb.

TABLE 9.—*Principal Lines of Arsenic Best Suited for Use in Analysis of Tin*

SPARK, SENSITIVE LINES

Wave Length, IA	Remarks
2860.46	Does not appear below 0.23 per cent As.
2780.23	Masked by Sn 2779.81.
2745.00	Masked by Fe 2746.486.
2349.84	Persists down to 0.03 per cent As. Suitable for measurement with Sn 2334.816.
2288.14	Not very sensitive. Liable to masking by Zn 2288.0.

ARC, SENSITIVE LINES

Wave Length, IA	Remarks
2860.46	Does not appear below 0.50 per cent As.
2780.23	Masked by Sn 2779.81.
2349.84	Most sensitive persisting down to 0.03 per cent As. May be measured against Sn 2334.816 as a standard.
2288.14	Masked by Fe 2289.0.

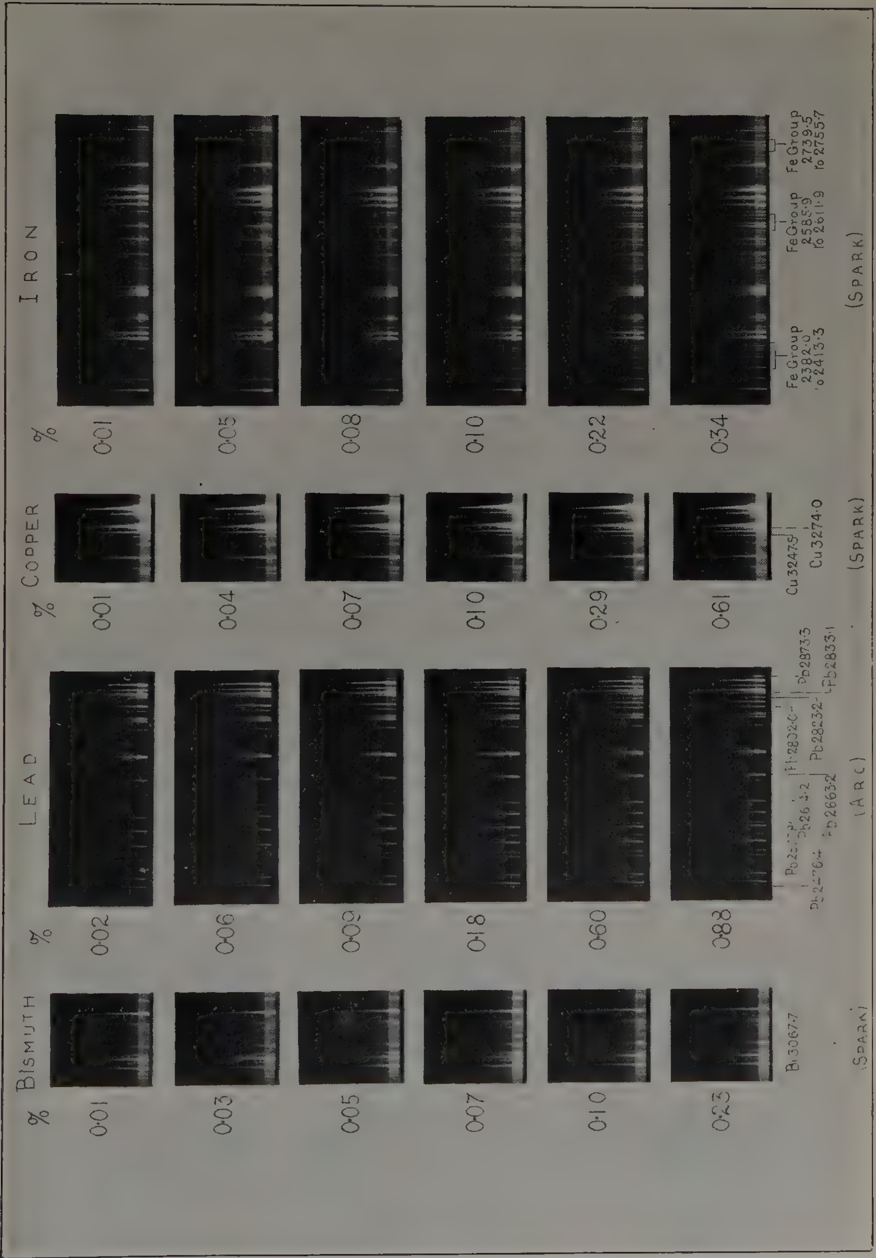

FIG 10.—SPECTROGRAMS.

The spectrograms shown in Fig. 10 were taken under identical experimental conditions and there is therefore perfect gradation in line intensities. A certain amount of finer detail is, of course, lost in reproduction.

Both antimony and arsenic are elements of poor spectroscopic sensitivity, and if it were found necessary to examine for these elements in small amounts, the only means of overcoming the difficulty would be to increase the time of exposure. This, however, would be better carried out in a separate spectrogram, as increase of the time of exposure would cause the lines of the other elements present to appear too strong for length measurements.

Fig. 9 shows the curves obtained for arsenic and antimony using spark emission, the line-pair $\frac{\text{As } 2349.84}{\text{Sn } 2334.816}$ being employed for the former element and $\frac{\text{Sb } 2311.50}{\text{Sn } 2317.22}$ for the latter. Arc emission cannot be recommended for the detection and estimation of these two elements.

CONCLUSION

By employing the spectrographic technique described, it has been possible to estimate bismuth, copper, lead, iron and zinc, occurring as impurities in tin, over such ranges as should meet ordinary industrial and commercial requirements. Owing partly to their poor spectroscopic sensitivity and partly to the masking of their most sensitive lines by those of other elements, arsenic and antimony cannot be estimated in amounts less than 0.03 and 0.07 per cent respectively.

The results obtained are summarized in Table 10, which indicates, for each metallic impurity, the number of determinations made, the approximate range of estimation and the errors incurred. The latter are stated in terms of *the total amount of the element present:* thus, a determination giving 0.11 per cent of an element as being present when there was actually

TABLE 10.—*Estimated Impurities in Tin*

Impurity	Spark					Arc				
	Approximate Range, Per Cent	Number of Determinations	Number of Cases in Which Error Exceeded			Approximate Range, Per Cent	Number of Determinations	Number of Cases in Which Error Exceeded		
			5 Per Cent	10 Per Cent	25 Per Cent			5 Per Cent	10 Per Cent	25 Per Cent
Zn........	0.02–1.00	9				0.02–1.00	9		1	
Cu........	0.02–0.30	10	1			0.03–0.60	11	1	1	
Bi........	0.01–0.30	10	1			0.01–0.30	10	3		
Fe........	0.01–1.00	11		1		0.01–1.00	11	1	3	
Pb........	0.01–1.00	13		2	1	0.01–0.35	11	2		
As........	0.03–0.50	7	1	1						
Sb........	0.07–0.50	4								
Totals............		64	3	4	1		52	7	5	0

only 0.10 per cent implies an error of 10 per cent. Out of a total of 64 estimations by spark emission, 8 instances occurred in which the error exceeded 5 per cent: in estimating by the arc there were 12 such instances out of a total of 52, and of these 5 exceeded 10 per cent.

The 96 cases where the error was less than 5 per cent require little comment beyond stating that under such circumstances the spectrographic method compares very favorably with, and in certain cases excels, the ordinary assay methods. From a standpoint of the reliability of the method, however, it is pertinent to inquire into the causes of the larger errors. Careful consideration of the experimental procedure showed that no blame could be attached either to the sector, spectrograph, or photographic technique, and it was equally clear that the analyses were not at fault. Further inquiry and investigation led the author to the conclusion that these larger errors arose from occasional inequalities in the light source, their origins differing with the form of emission employed.

In the case of the spark, the small variations in electrical conditions were quite insufficient to account for these larger errors and their cause appears to be due to occasional small-scale segregation of the elementary impurity, the effect of which is rendered appreciable by reason of the small surface of the sample from which sparking actually takes place. The chief factor involved in bringing about such segregation is doubtless the gravitational sinking of early formed crystals of the impurity, or a phase containing it, in the still-molten metal. Thus the high specific gravity of lead (11.34) compared with that of tin (7.30) coupled with the practically complete insolubility of lead in the latter metal would seem to account for the increase in the number of determinations where the errors exceeded 10 per cent (3 out of 13). Zinc presents an interesting contrast to lead in this respect, for here the specific gravities of the two metals (tin and zinc) are almost identical and Curry[19] has found that all tin-zinc alloys containing less than 5 per cent of zinc are homogeneous under the microscope—an observation which is in harmony with the satisfactory results obtained for this element. Opportunity for segregation of small amounts of copper and bismuth to occur in tin exists, but on the whole does not appear to be so great as the opportunity for segregation of lead.

Stead[20] who investigated the ternary alloys of tin, arsenic and antimony, discovered that all alloys of tin and antimony containing less than 7.5 per cent of antimony crystallize in the same arborescent forms as pure tin, the crystallites of tin containing SnSb in solid solution. The behavior of tin-arsenic melts was totally different, there being a tendency to segregation by reason of the formation of tin-arsenide, Sn_3As_2, crystals of which compound floated to the surface of the molten metal. The somewhat erratic results obtained with a tin sample of high arsenic content might be ascribed to such a cause.

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[19] B. E. Curry: *Jnl.* Phys. Chem. **13,** 589.

[20] Stead: *Jnl.* Inst. Metals (1919) **22,** 127.

From the above considerations it is evident that, in order to realize the full accuracy of which the spectrographic method is capable, precautions should be taken to avoid small-scale segregation in the preparation of the sample bars. These may be effected by casting in a chilled mold and, if time permits, by subsequent annealing for a short period. As a further check, it is recommended that at least two spectrograms be taken of the same sample, the greater certainty which this affords being well worth the extra two or three minutes required.

In employing arc emission, the possibility of error due to segregation does not enter, since the metal is here in the molten condition. The larger errors in this instance are doubtless caused by fluctuations in the electrical conditions which are far more difficult to control[21] than in connection with the spark.

Experience gained during the present investigation led the author to regard the spark as a more satisfactory form of emission than the arc for estimating the impurities in tin. While it is true that most elements are more sensitive in the arc and that, from a commercial point of view, this form of emission is cheaper and more convenient than the spark, it suffers from two disadvantages: (1) the difficulty of controlling electrical conditions, noted above, and (2) the fact that the highly sensitive lines in the arc spectrum of iron seriously interfere with the detection and estimation of the other elements. Moreover, it was found that the estimation of copper was less satisfactory by the arc, and it was also unsuitable for arsenic and antimony. For these reasons, therefore, spark emission is to be preferred for more precise work although the arc might prove useful when only an approximate analysis is required, or when it is merely necessary to ascertain whether a given element is present in amounts much above or below a stipulated percentage.

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[21] It has subsequently been found that self-inductance, placed in series in the arc circuit, exerts a considerable steadying influence.

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